8th Annual Ammonia Fuel Conference

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Reforming and burning of ammonia in micro hydrogen and power generation systems

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Acknowledgment:

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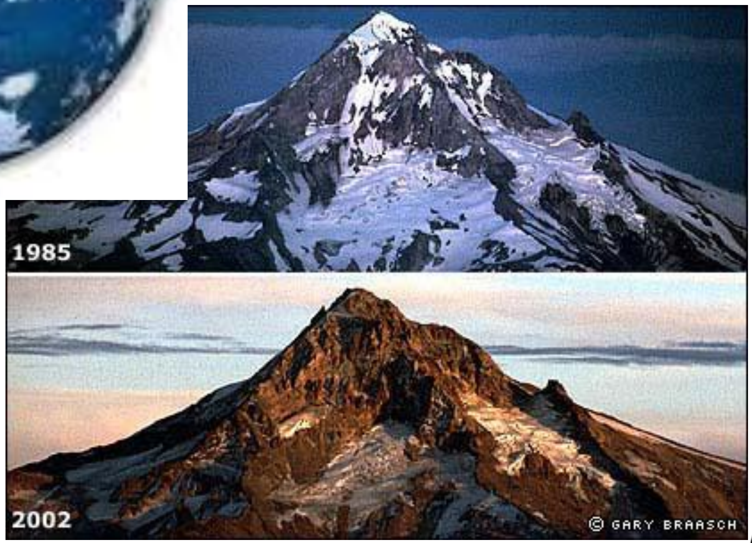
Sungkyunkwan University & ME

- **Sungkyunkwan Univesity:**
  - The oldest university in Korea, founded in 1398.
  - One of the leading universities, among the top 4 in Korea.
  - Private university strongly supported by Samsung.
- **School of Mechanical Engineering:**
  - Established in 1967.
  - Natural sciences campus.
  - Faculties: 33.
  - Undergraduate students: 727.
  - Graduate students: 135.

Global warming



CO_2 emissions in Korea

- **Korea Metrological Administration report (2011): the average amount of CO_2 at the national air monitoring station in Anmyeondo, Chungcheong Province, in 2010 was 394.5 ppm:**
  - **Korea's CO_2 level has been on the rise for eleven straight years since 1999 when the amount was 370.2 ppm.**
  - **The U.S. Center for Global Development (2007): Korea ranked 10th among the world's greenhouse gas emitters by emitting 185 million tons of such gases annually.**
  - **The average temperature in Korea has risen by 1.5 degrees over the last 100 years.**

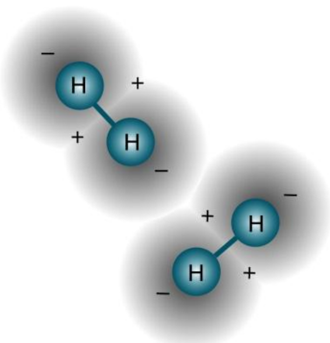
- **The Kyoto Protocol in 1997:**
  - **Under the second phase of the Protocol, Korea may be required to reduce greenhouse gas emissions between 2013 and 2017.**
  - **In order to reduce 5% of greenhouse gas emissions in 1995, the estimated cost is 8 billion US dollars.**

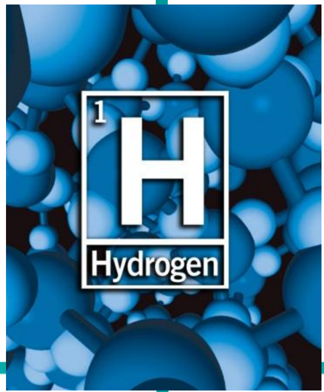
Hydrogen (H_2)

Clean (Carbon-free)

Energetic (120 MJ/kg)

Abundant (Renewable)





Wide flammability limits

Low ignition energy

High burning velocity

Hydrogen (H_2)

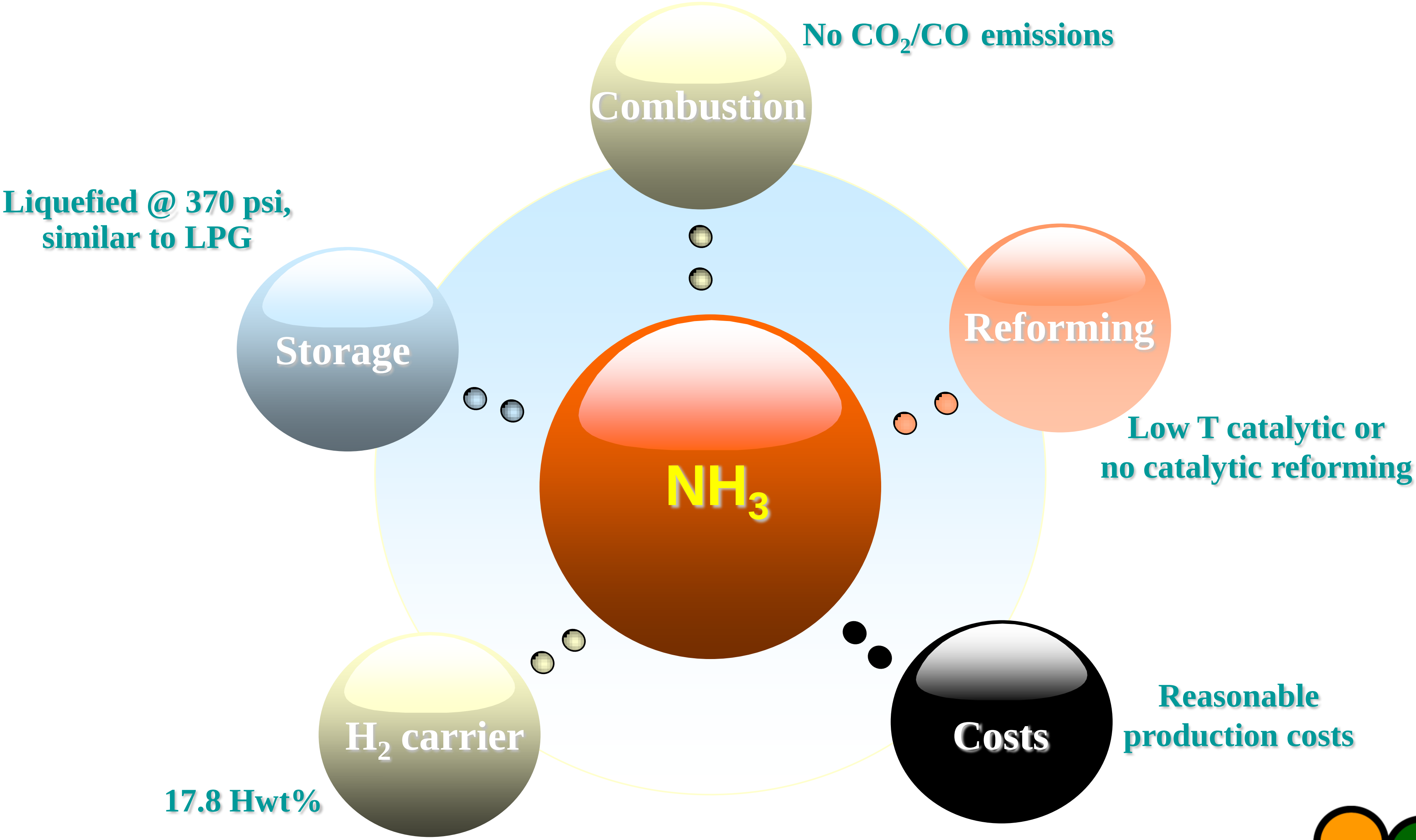
Mass production

Difficulties of transport/storage
Pipelines: infrastructure needed

On-site production

No transport problem if hydrocarbons used
But CO_2/CO emitted

Ammonia (NH_3)



Combustion
No CO2/CO emissions
Reforming
Low T catalytic or
no catalytic reforming
Storage
Liquefied @ 370 psi,
similar to LPG
NH3
H2 carrier
17.8 Hwt%
Costs
Reasonable
production costs

Ammonia (NH_3)

Fuel/system	ε_r (%)	\$ 100 km^{-1}	Range (km)
Gasoline/ICE	24	6.06	825
CNG/ICE	28	6.84	292
LPG/ICE	28	5.10	531
Methanol/reforming + fuel-cell	33	9.22	376
H_2 metal hydrides/fuel-cell	40	4.40	142
NH_3/direct ICE	44	1.57	592
NH_3/Th decomp, ICE	28	2.38	380
NH_3/Th decomp Sep, ICE	31	2.15	420
NH_3/direct FC	44	1.52	597
NH_3/Th. decomp + Sep, FC	46	1.45	624
NH_3/electrolysis	20	3.33	271

- **Zamfirescu C, Dincer I, "Using ammonia as a sustainable fuel," J Power Sources 185 (2008), 459-465.**

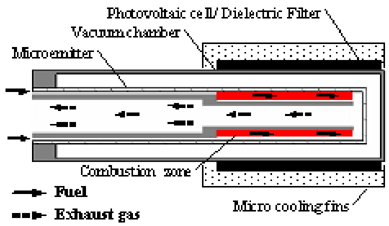
Ammonia in Korea

No earlier works for use of ammonia as a fuel

- Ammonia has been used for various fields during the last 50 years in Korea:
  - Fertilizers, refrigerants, catalysts and process chemicals.
  - Safety issues associated with handling of ammonia resolved.
  - Related regulations: industrial safety and health regulations and high pressure gas safety regulations.
- Ammonia is cheaper than other fuels; however, 100% imported due to low demand in Korea.

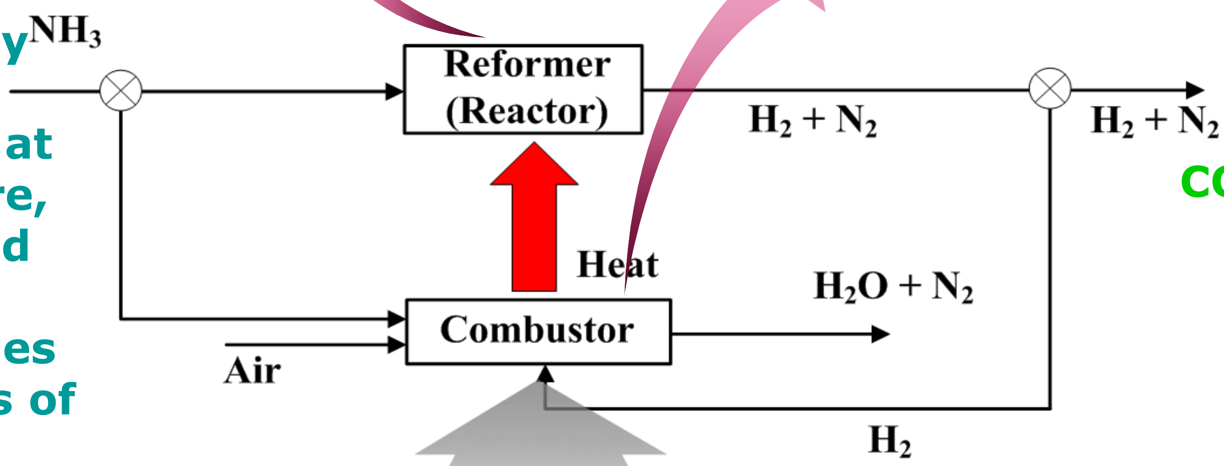
Use of ammonia as a fuel

Catalytic or thermal dissociation

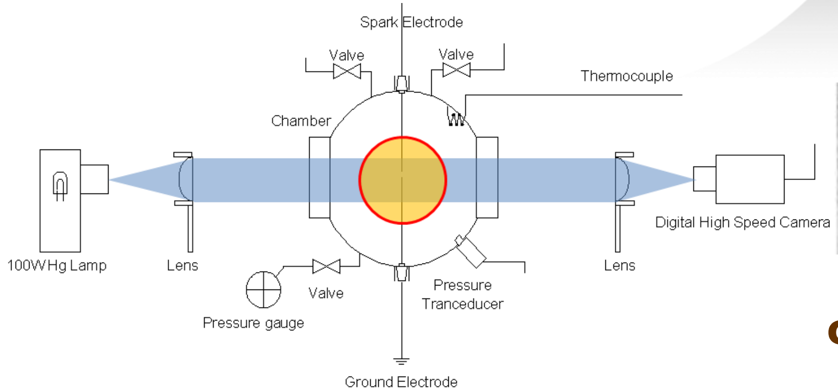


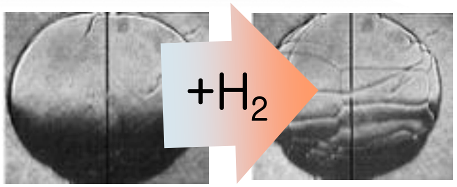
Heat recirculation

Use of outwardly propagating spherical flames at constant pressure, burner-stabilized flames and counterflow flames for measurements of fundamental parameters



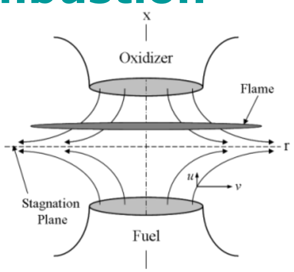
CO_2/CO free



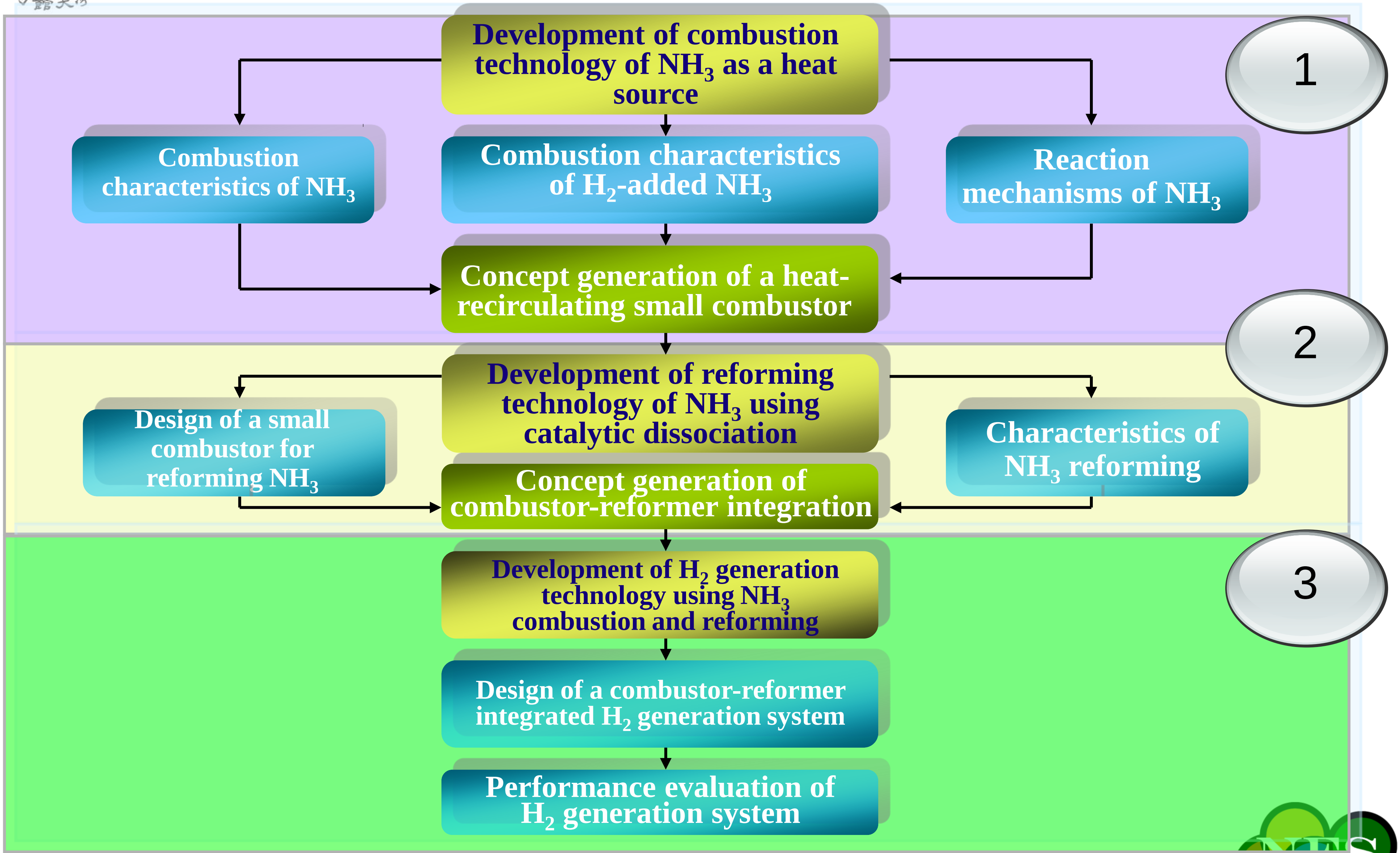


NH_3 combustion

H_2-added NH_3 combustion



Ammonia as a fuel (2008-2011)



Technological challenges to overcome

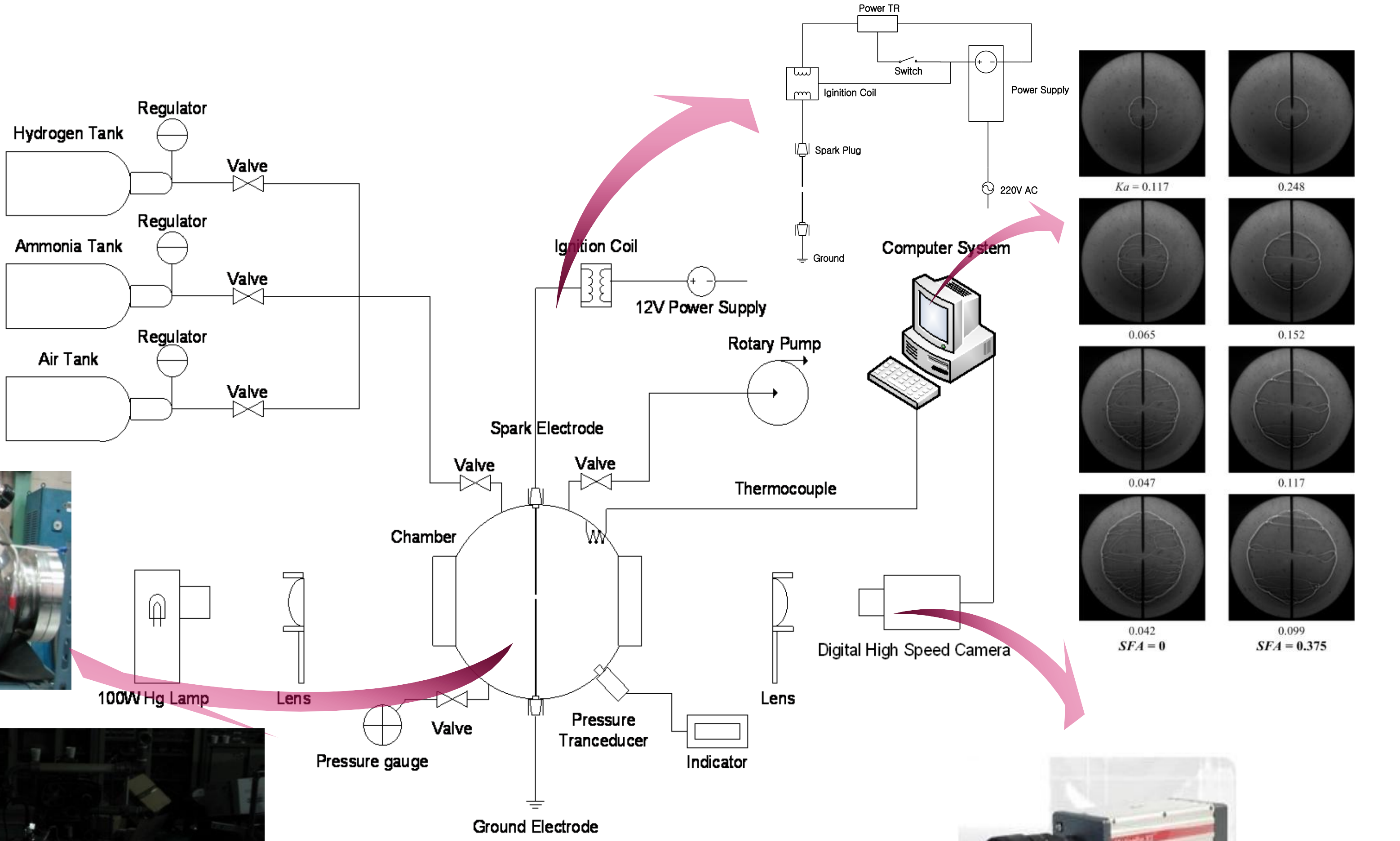
- **Micro-combustor:**
  - Burning temperature high enough for combustion stability and performance but suppressing NO_x formation
  - Heat losses quenching flames
  - Ignition (delay)
  - Heat recirculation concept and H_2 addition applied

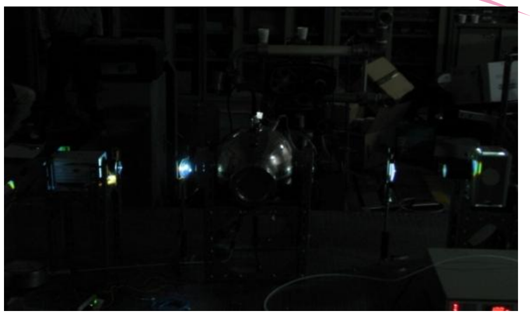
- **Micro-reformer:**
  - Uniform and steady heating: residence time and array
  - Erosive to some materials such as metals

- **Combustor-reformer integrated system:**
  - Effective heat transfer between a combustor and a reformer
  - Simple structure with heat recirculation

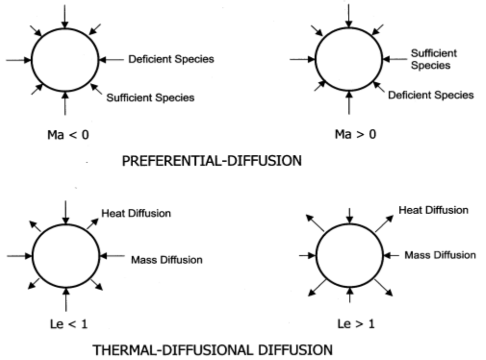
Burning ammonia - summary

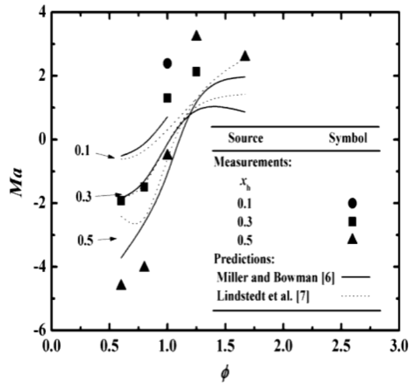
Fundamental characteristics: spherical flames

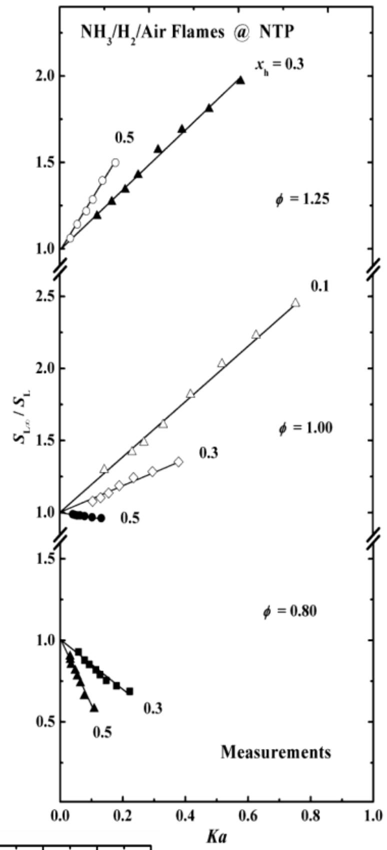


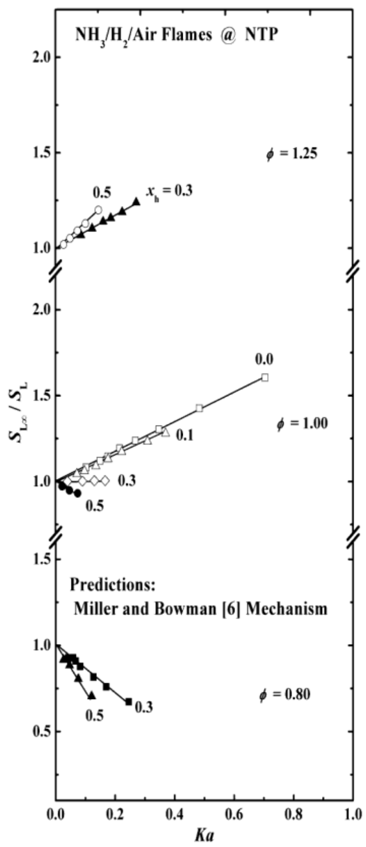


Fundamental characteristics: spherical flames







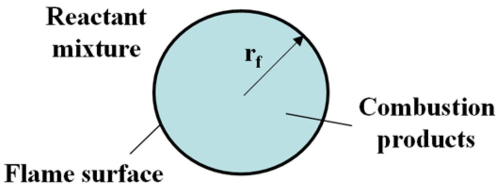


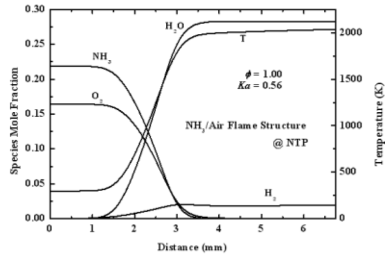
- **Laminar burning velocity**

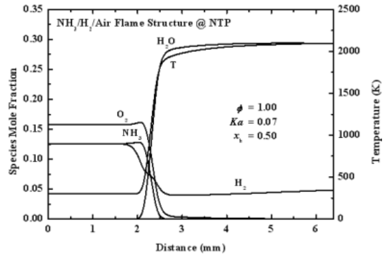
$$S_L = (\rho_b/\rho_u)\, dr_f/dt$$

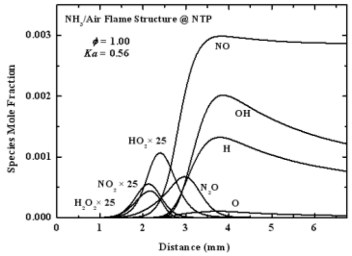
- **Flame stretch**

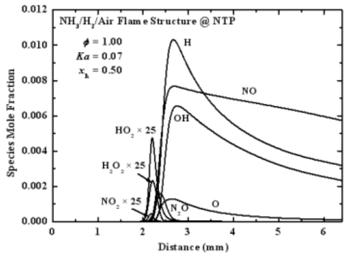
$$K = (2/r_f)\, dr_f/dt$$

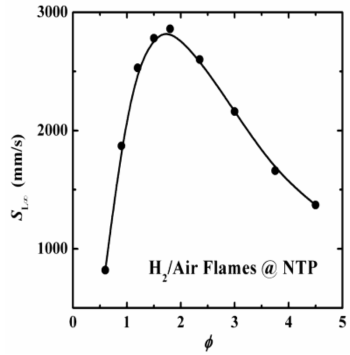










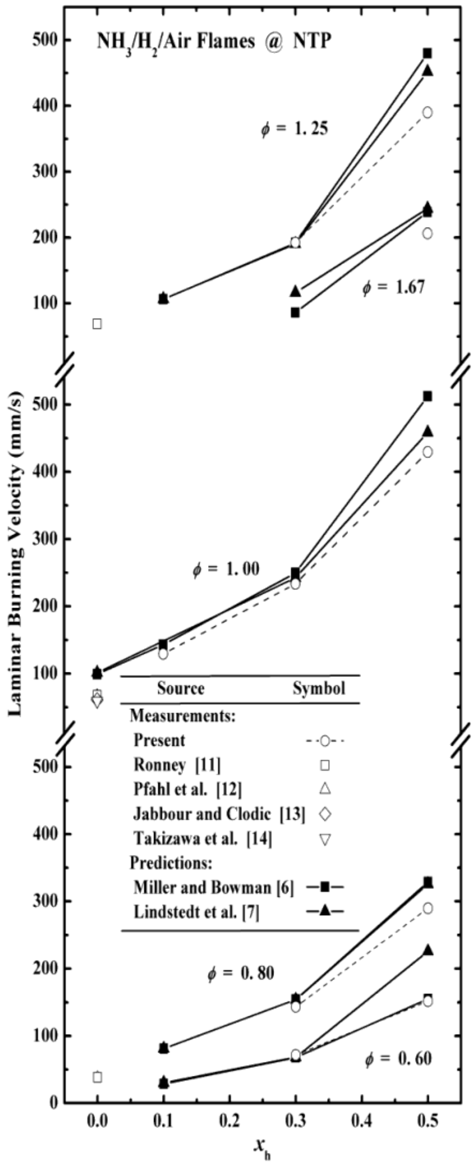


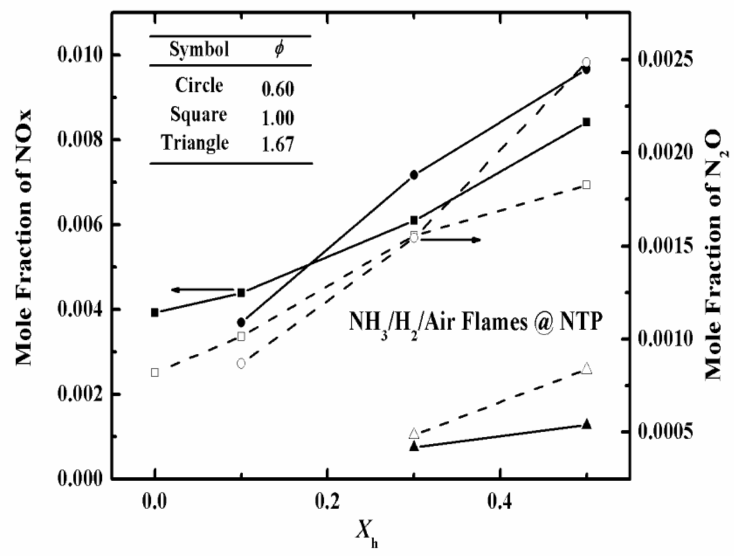
$$S_L = S_{L\infty} - LK \quad (1)$$

$$S_{L\infty}/S_L = 1 + Ma\, Ka \quad (2)$$

$$Ka = K\,\delta_D/S_L, \quad Ma = L/\delta_D, \quad \delta_D = D_u/S_L \quad (3)$$

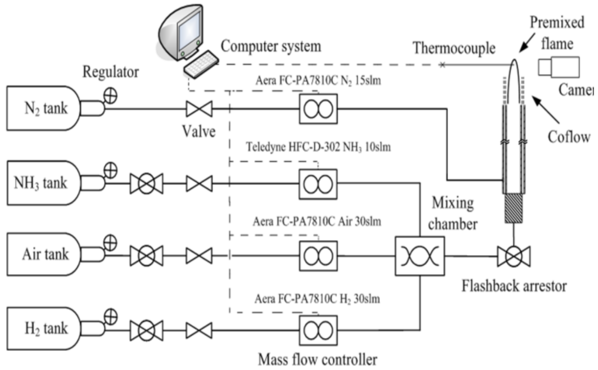
Fundamental characteristics: spherical flames

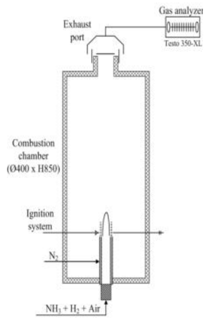


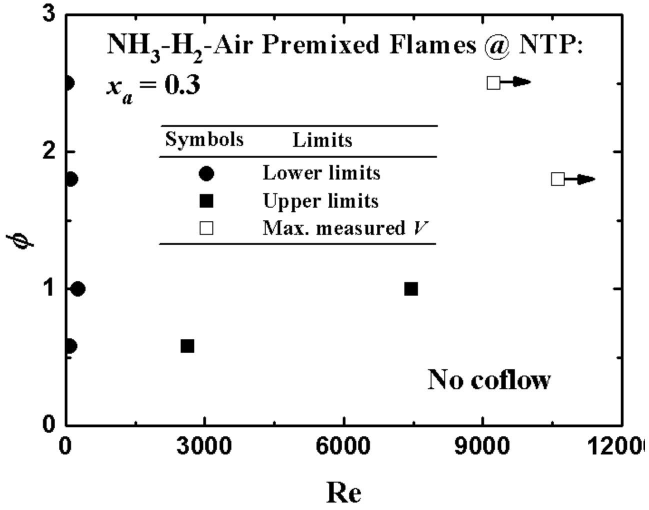


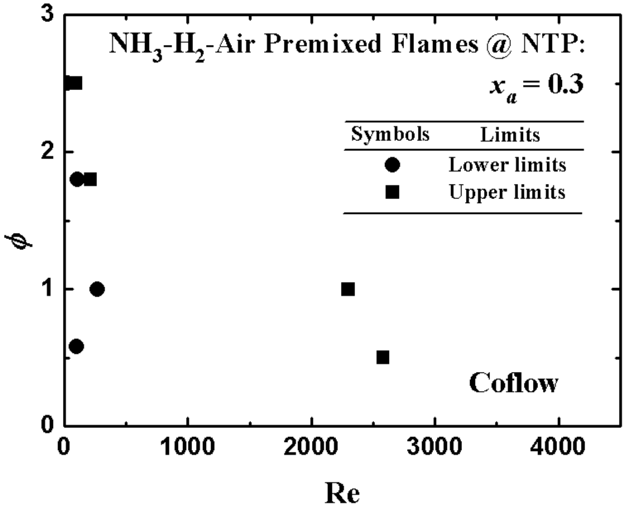
- **Hydrogen substitution improves the burning performance with relatively low NO_x and N_2O emissions in fuel-rich ammonia/air flames.**

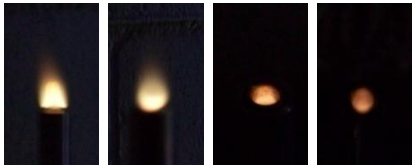
Fundamental characteristics: burner-stabilized flames





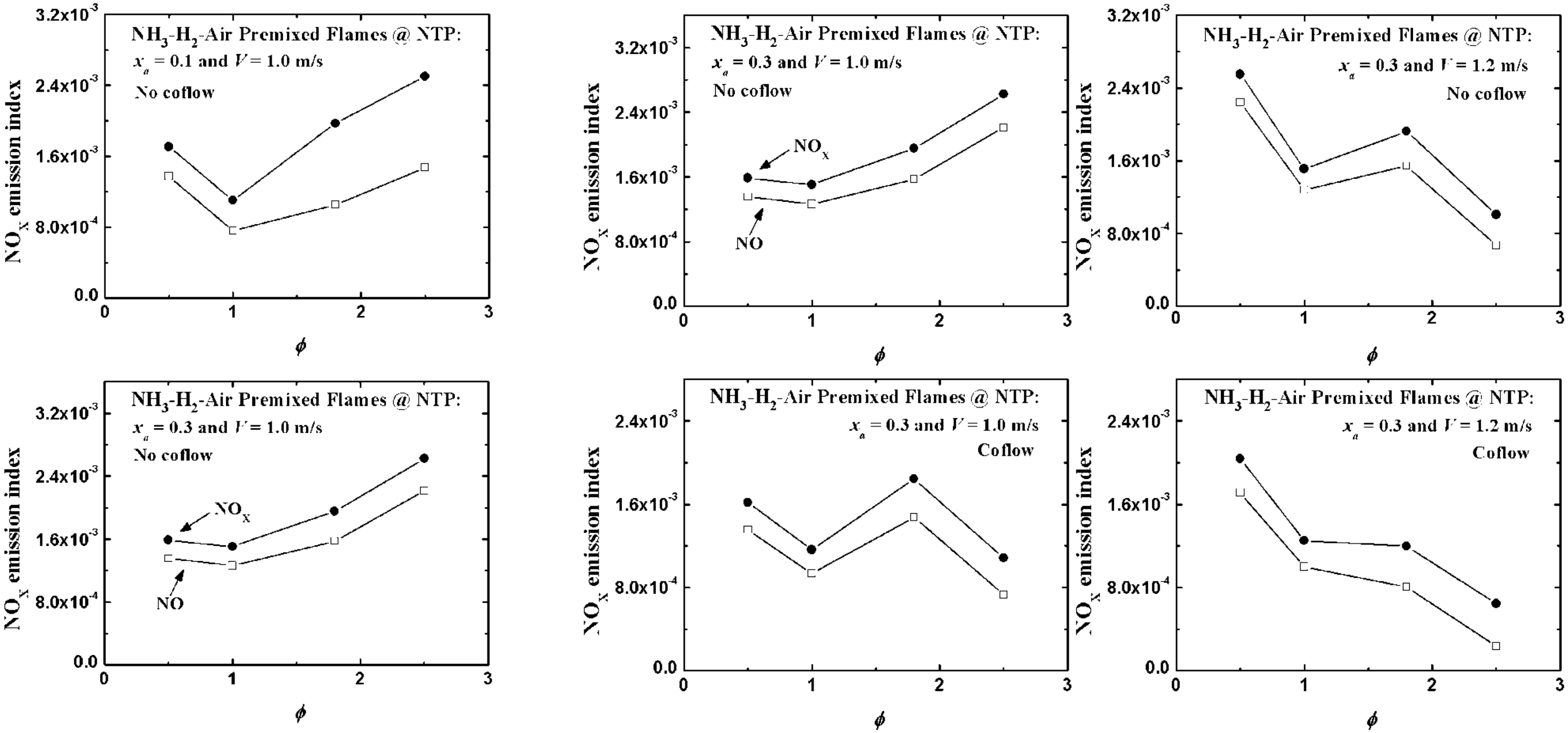






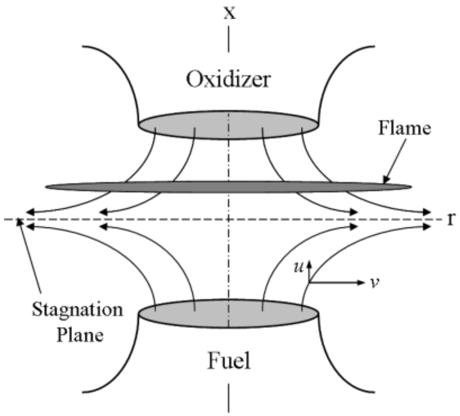
- The lower stability limits due to heat losses, while the upper stability limits due to insufficient residence times of injected mixture jet.
- Reduction of the stability limits with NH_3 substitution in H_2/air flames.
- Opposite tendencies of the upper stability limits with and without the coflow.

Fundamental characteristics: burner-stabilized flames



- Ammonia substitution enhances the NO_x formation in general; however, the NO_x emission index is almost constant with the enhanced ammonia substitution.
- At fuel-rich conditions, the NO_x emission index is reduced with increasing burner exit velocities of the injected mixtures.

Fundamental characteristics: counterflow nonpremixed flames



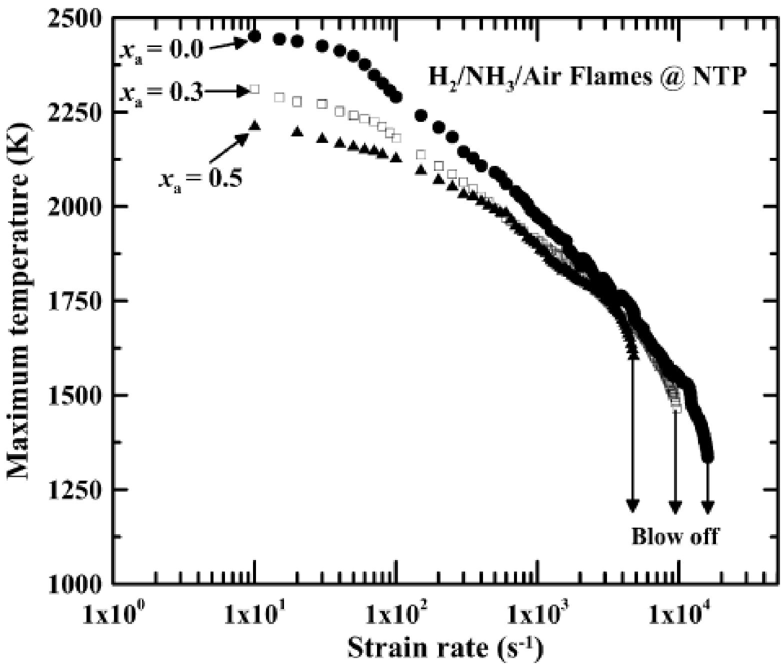
- **Governing equations**
  - Continuity $G(x)=\frac{dF(x)}{dx}$
  - Momentum $H-2\frac{d}{dx}\left(\frac{FG}{\rho}\right)+\frac{3G^2}{\rho}+\frac{d}{dx}\left[\mu\frac{d}{dx}\left(\frac{G}{\rho}\right)\right]=0$
  - Energy $\rho u\frac{dT}{dx}-\frac{1}{c_p}\frac{d}{dx}\left(\lambda\frac{dT}{dx}\right)+\frac{\rho}{c_p}\sum_{k=1}^{K}c_{p_k}Y_kV_k\frac{dT}{dx}+\frac{1}{c_p}\sum_{k=1}^{K}h_k\dot{w}_k-\frac{\dot{q}_r}{c_p}=0$
  - Species $\rho u\frac{dY_k}{dx}+\frac{d}{dx}(\rho Y_kV_k)-\dot{w}_k=0,\quad k=1,\ \dots,\ K$

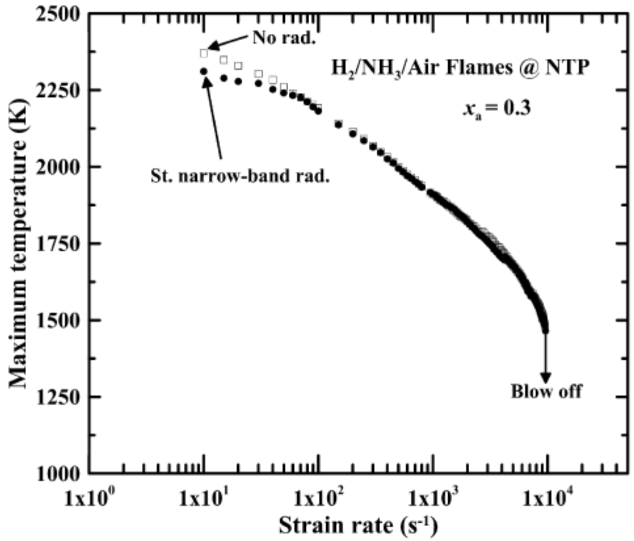
  where, $G(x)\equiv-\frac{\rho v}{r}$ $F(x)\equiv\frac{\rho u}{2}$ $H\equiv\frac{1}{r}\frac{\partial p}{\partial r}=\text{constant}$

- **Boundary conditions** $x=0:\ F=\frac{\rho_Fu_F}{2},\ G=0,\ T=T_F,\ \rho uY_k+\rho Y_kV_k=(\rho uY_k)_F$

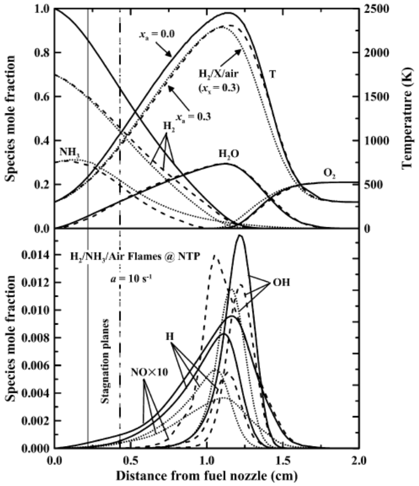
  $x=0:\ F=\frac{\rho_Ou_O}{2},\ G=0,\ T=T_O,\ \rho uY_k+\rho Y_kV_k=(\rho uY_k)_O$

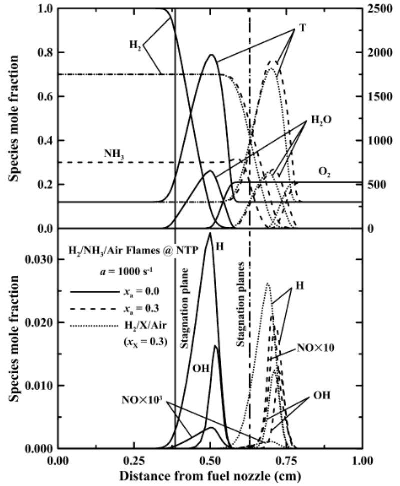
- **Strain rate** $a=\frac{-2u_O}{L}\left[1-\frac{u_F}{u_O}\sqrt{\frac{\rho_F}{\rho_O}}\right]$

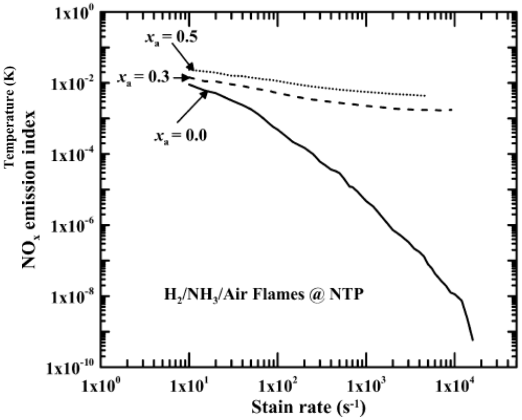


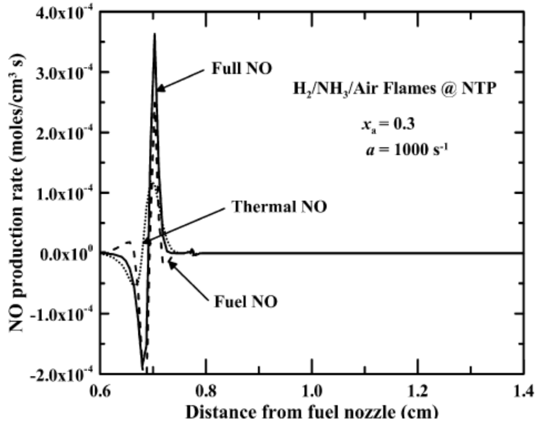


Fundamental characteristics: counterflow nonpremixed flames





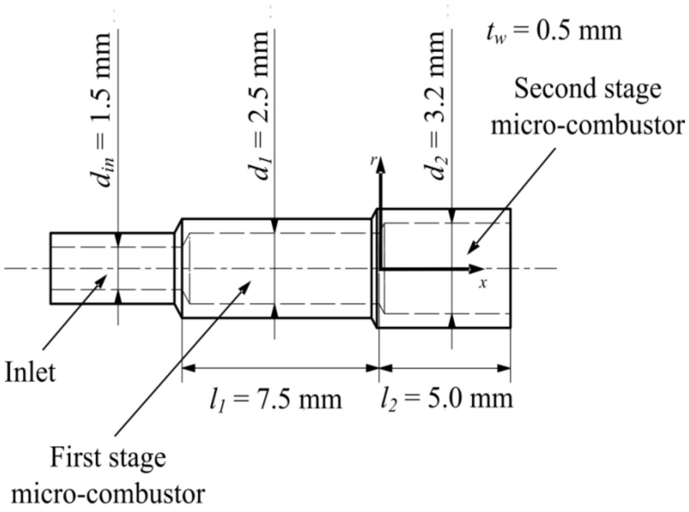


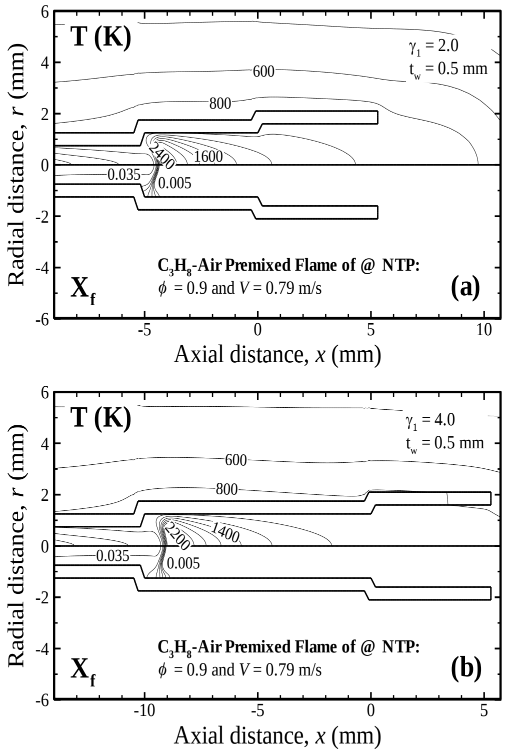


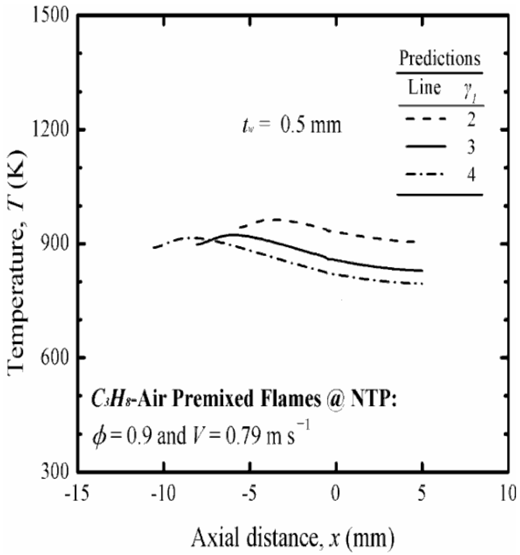
- Ammonia is all capable to significantly reduce the high-stretch extinction limits, the maximum flame temperature and the concentration of light radicals with ammonia substitution in hydrogen/air flames.
- The remarkable reduction of temperature with NH_3 substitution at low strain rates is observed due to the effect of the less reactive NH_3 substitution, while the insignificant reduction of temperature at high strain rates is observed due to the effect of pure stretch regardless of NH_3 substitution.
- Chemical effects (rather than thermal effects) of NH_3 substitution on flame structure are dominant.

Design of micro-combustors

- **In order to satisfy the primary requirements for designing the micro-combustor integrated with a micro reforming system (stable burning in the small confinement, maximum heat transfer through the walls and uniform temperature distribution along the wall surface), the micro-combustor that is simply cylindrical to be easily fabricated but two-staged, expanding downstream was designed.**







Design of micro-combustors

- **Preliminary tests of the two-staged micro-combustor for micro reforming systems were conducted for a methanol-steam reforming system the reforming characteristics of which are relatively well known:**
  - **Improved performance compared to earlier micro methanol-steam reforming systems.**
  - **But gaseous ammonia reforming does not need a micro-evaporator.**

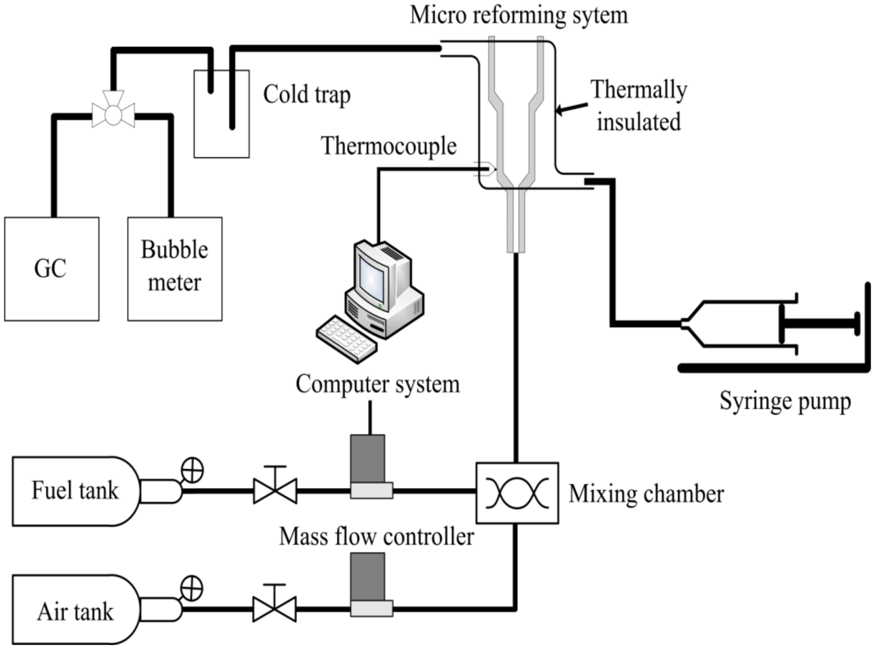
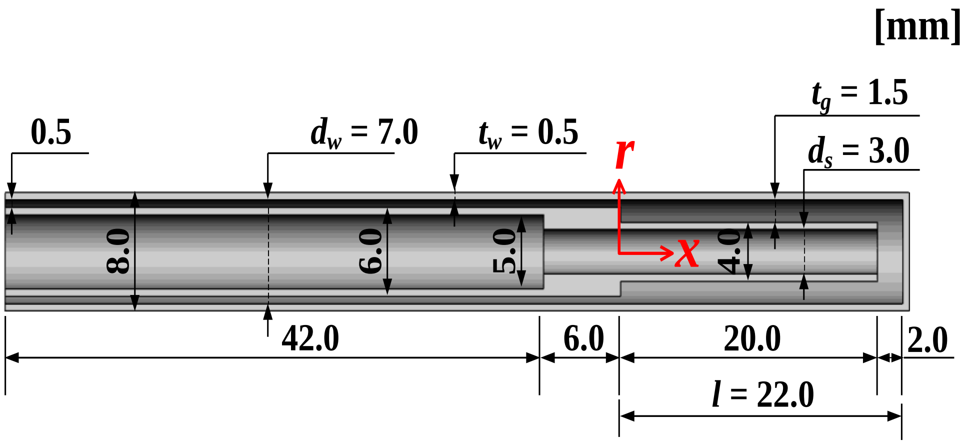


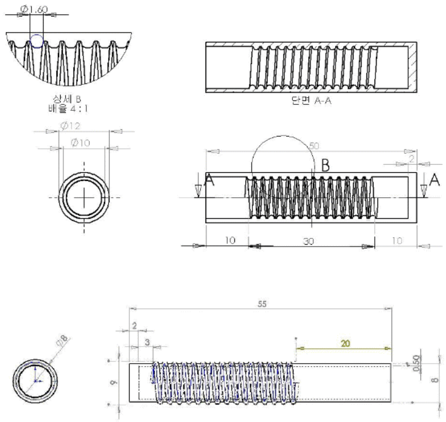
Table 1 – Optimized operating conditions and performance of micro reforming system.

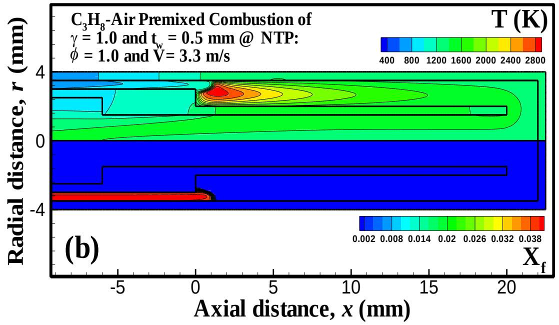
Operation/performance parameters	Values
Materials	Stainless steel (SS304)
Equivalence ratio of pre-mixed propane–air flame (ϕ)	1.0
Micro-combustor inlet velocity (V)	0.78 m/s
Molar ratio of water to methanol (S/C)	1.38
Feed rate of methanol–water mixture ($\dot{m}_f$)	0.10 ml/min
Production rate of reformed gas ($\dot{m}_r$)	53.6 ml/min = 6.9 W (based on LHV)
Conversion rate of methanol ($\dot{r}$)	97.5%
Carbon monoxide emissions ([CO])	6.7 ppm
Overall system efficiency (η)	39.7%

Design of micro-combustors

- A micro-combustor that burns gaseous fuel-air mixtures as a heat source has been designed:
  - A cylinder with an expanded exhaust outlet that facilitates ignition and an annular-type shield that adopts a heat-recirculation concept.





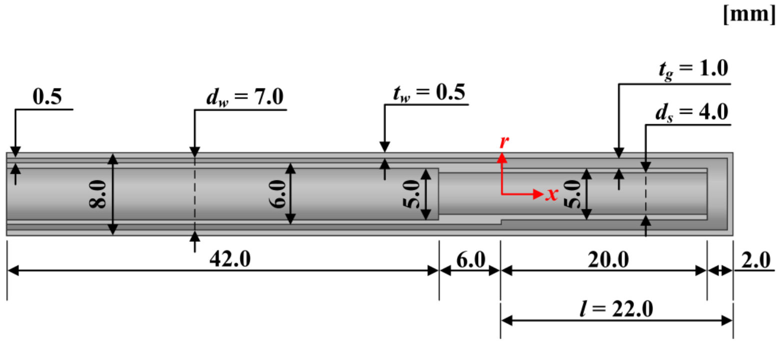


Reforming ammonia

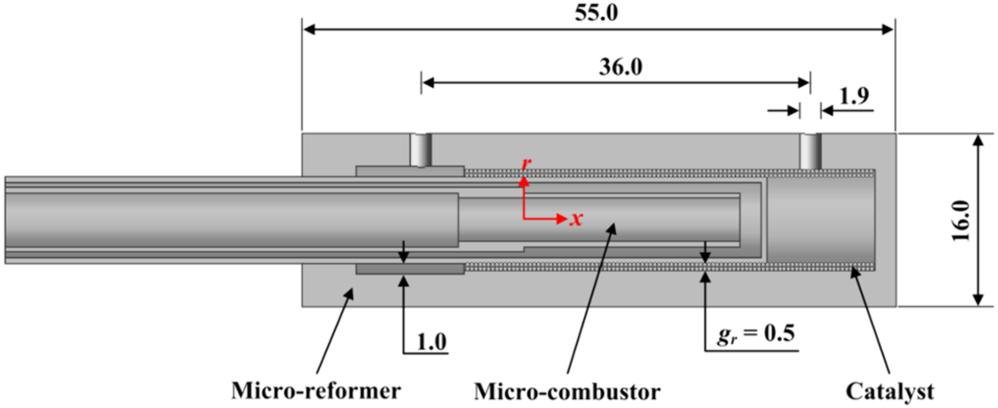
Objectives

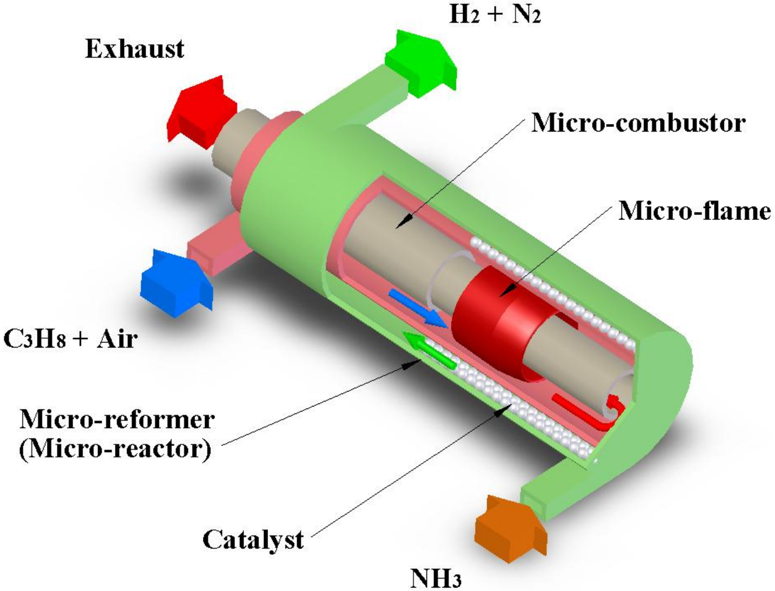
- **Study the potential of using NH_3 as a clean fuel, particularly for portable H_2-generation systems:**
  - **Determine a basic configuration of the micro-reformer system, including the heat-recirculating micro-combustor that can feasibly control stable burning and enhance the overall system efficiency and using the catalytic reforming process.**
  - **Observe the effects of operating parameters (the feed rate of NH_3 and the micro-combustor inlet velocity of fuel-air mixtures) on the performance of the micro-reformer system (the production rate of reformed gas, the conversion rate of NH_3 and the overall system efficiency).**
  - **Observe the effects of varying the micro-reformer catalyst materials on the performance of the micro-reformer system, considering the cost-effective candidates.**
  - **Identify the optimized design and operating conditions from the observations.**

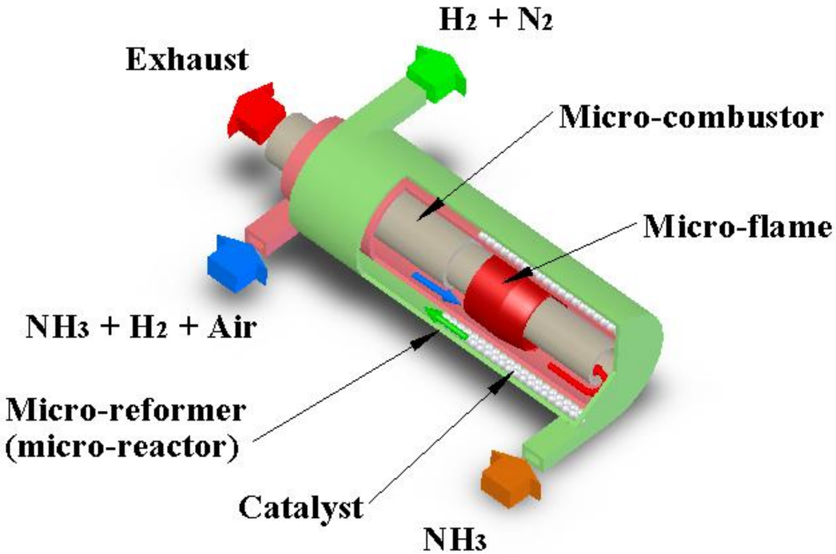
Experimental methods



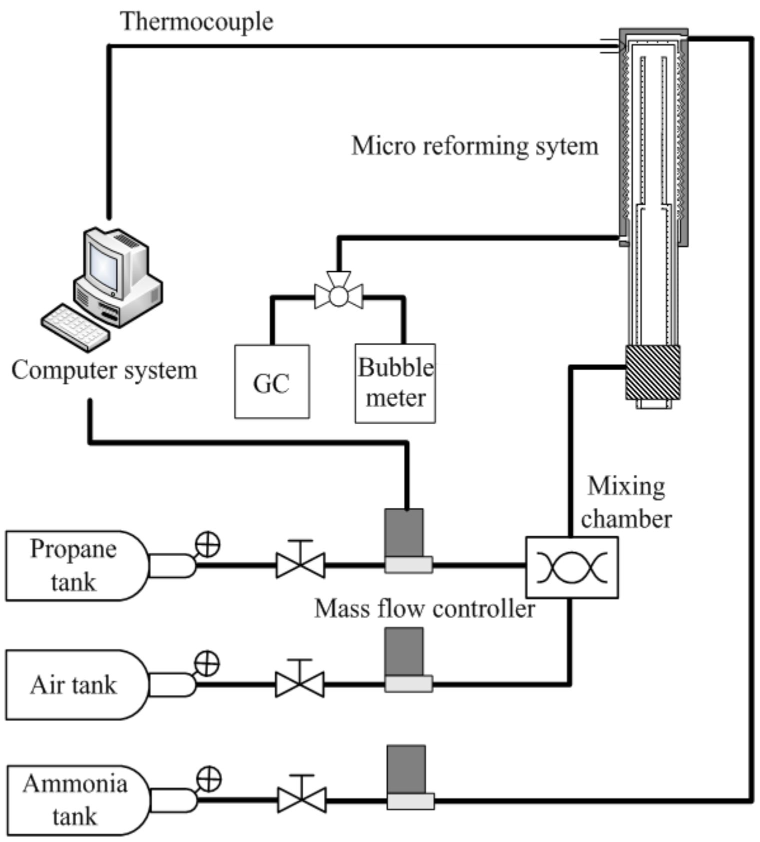
$$2NH_3 \longleftrightarrow 3H_2 + N_2$$





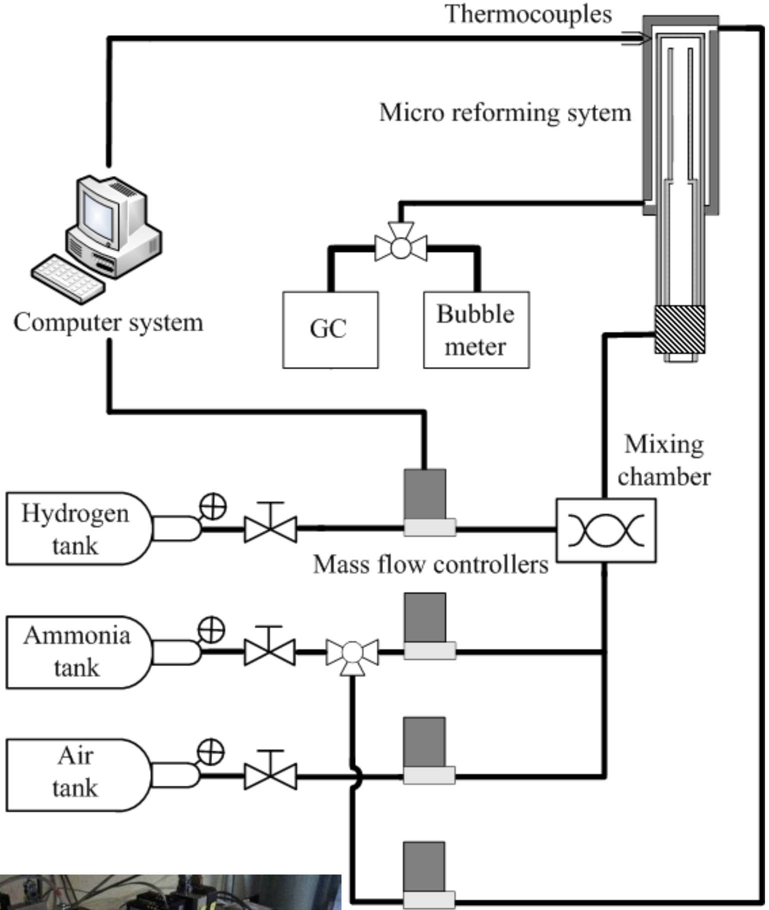


Experimental methods (C_3H_8-air)



- **Test micro reforming system (SS304)**
- **Gaseous fuel-air mixture supply system (MFCs: 0–2,000 sccm, accuracy of ±1.0% of full-scale)**
- **Gaseous NH_3 feed system (MFCs)**
- **Bubble meter and gas chromatography (Agilent 6890)**
- **Thermocouples (K-type)**
- **Micro-reformer catalysts: Ru (baseline), Ir and $Ni/SiO_2/Al_2O_3$**
- **Test conditions (micro-combustor):**
  - **V = 2.6–4.1 m/s, ϕ = 1.0**
  - **C_3H_8 @ NTP (micro-combustor)**

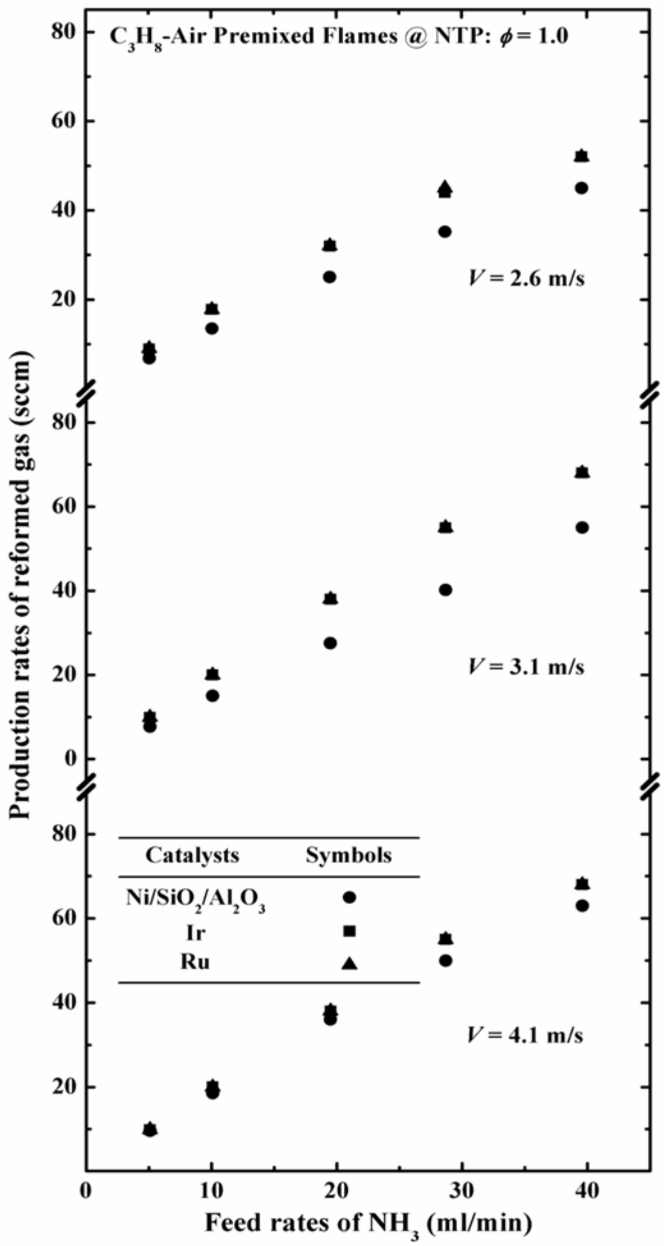
Experimental methods (NH_3-H_2-air)



- Test micro reforming system (SS304)
- Gaseous sccm, accuracy of ±1.0% of fuel-air mixture supply system (MFCs: 0–2,000 full-scale)
- Gaseous NH_3 feed system (MFCs)
- Bubble meter and gas chromatography (Agilent 6890)
- Thermocouples (K-type)
- Micro-reformer catalysts: Ru
- Test conditions:
  - V = 1.5–3.0 m/s, ϕ = 0.8–1.25
  - X_h= 0.3–0.5
  - NH_3/H_2 @ NTP (micro-combustor)
  - $\dot{m}_f$ = 10 ml/min (micro-reformer)

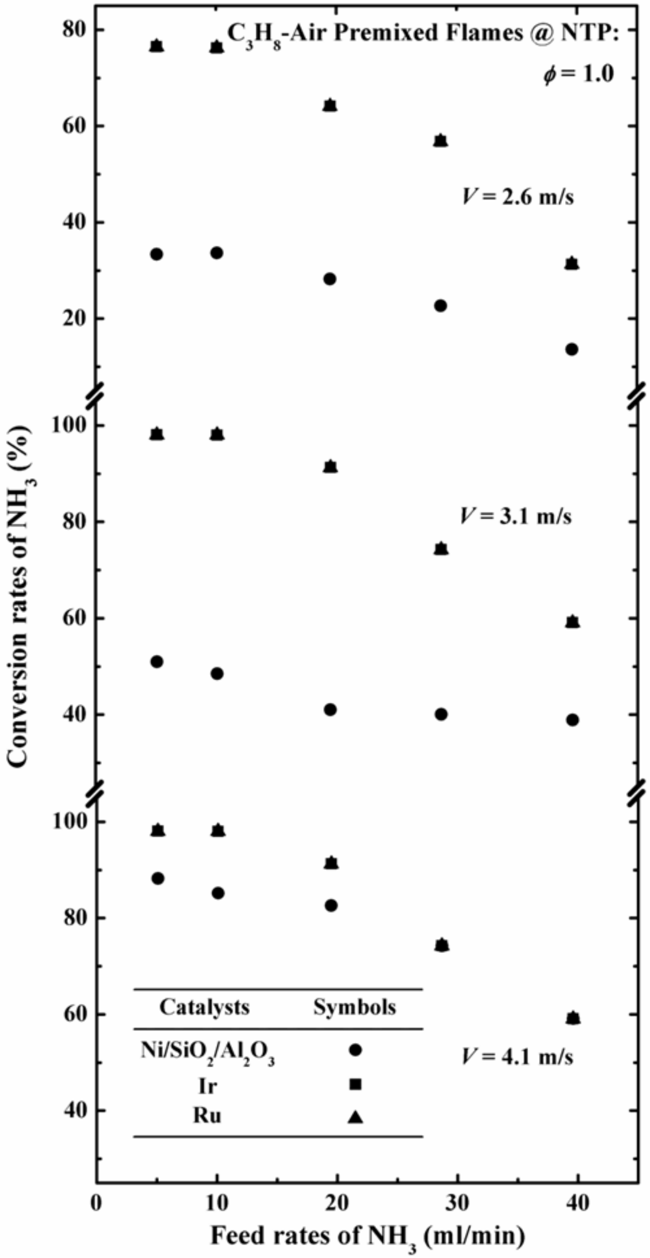
Production rate of reformed gas (C_3H_8-air)

- Ru, Ir and $Ni/SiO_2/Al_2O_3$ catalysts were considered.
- Production rates of reformed gas increase as feed rates of ammonia increase.
- For $Ni/SiO_2/Al_2O_3$, higher temperature condition in the micro-reformer (and hence in the micro-combustor) than that for Ir and Ru is needed.



Conversion rate of ammonia

- The conversion rate increases with increasing V until V = 3.1 m/s for Ir and Ru.
- For $Ni/SiO_2/Al_2O_3$, $\dot{r}$ increases with increasing V up to V = 4.1 m/s.
- The maximum value of $\dot{r}$ for Ir and Ru is 98.0 % at $\dot{m}_f$ = 5.0-10.0 ml/min and V = 3.1-4.1 m/s.

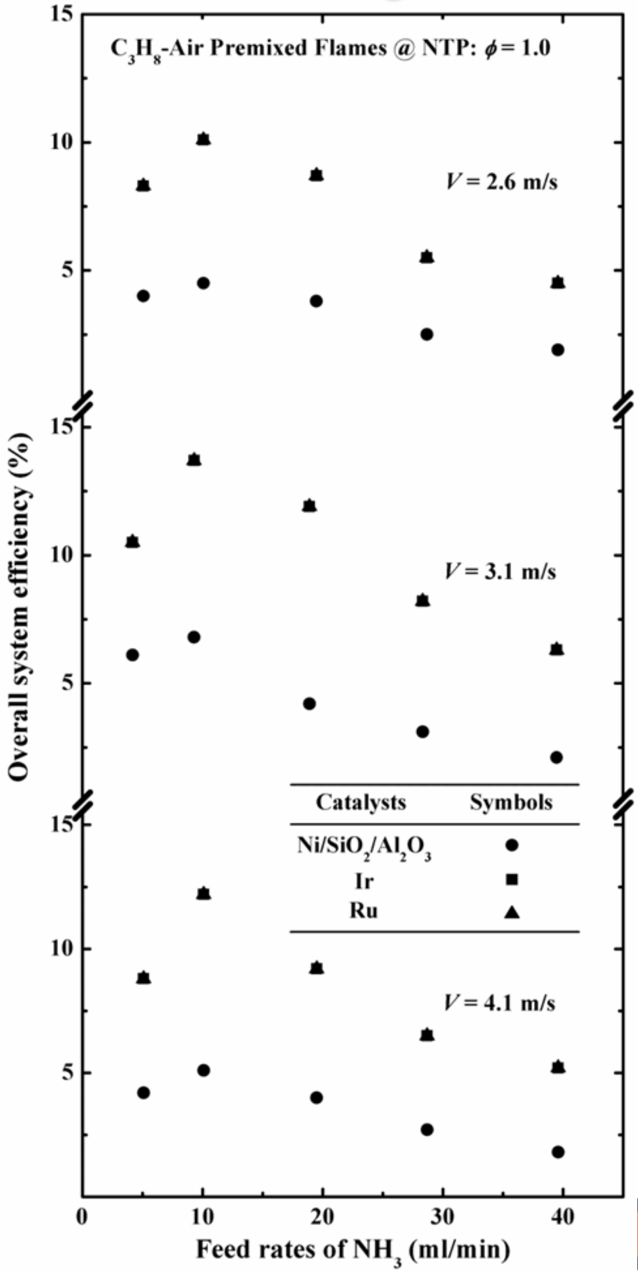


Overall system efficiency

- The maximum overall system efficiency is observed at $\dot{m}_f$ = 10.0 ml/min and *V* = 3.1 m/s:
  - $\dot{m}_f$ < 10.0 ml/min: $\dot{m}_r$ is too small.
  - $\dot{m}_f$ > 10.0 ml/min: not enough residence time.

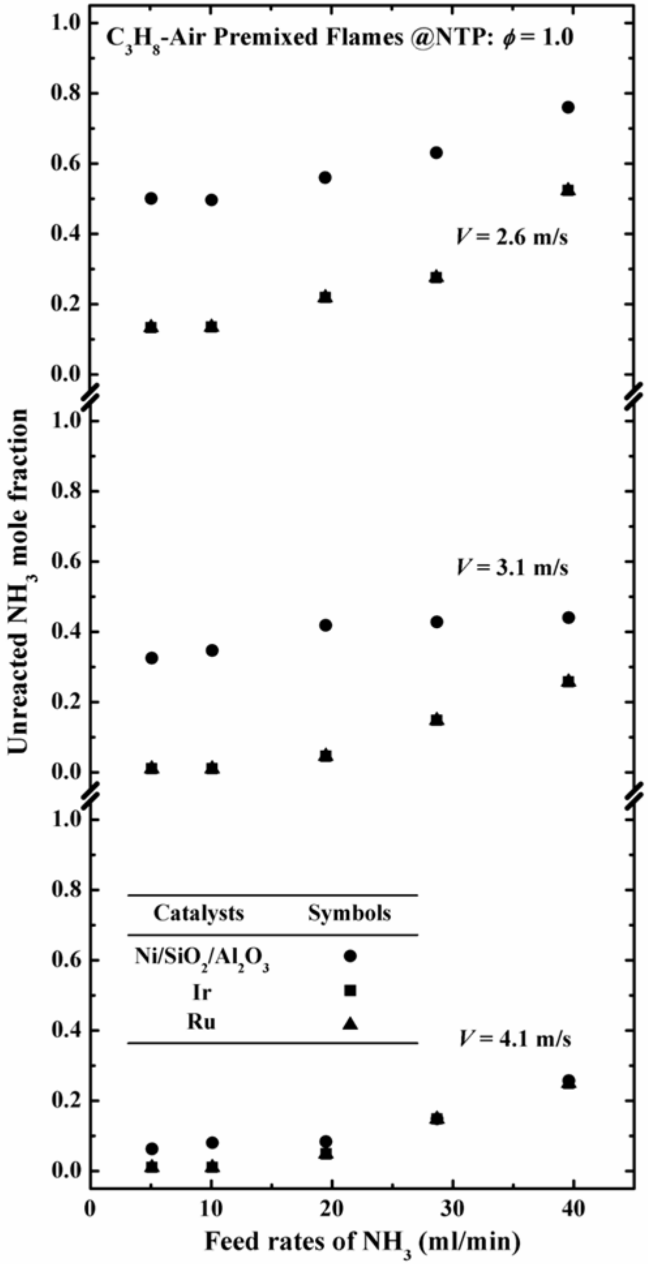
- The overall system efficiency for $Ni/SiO_2/Al_2O_3$ is lower than that for Ru and Ir under all the present conditions.

- The maximum overall system efficiency is 13.7%.



Unreacted ammonia mole fraction

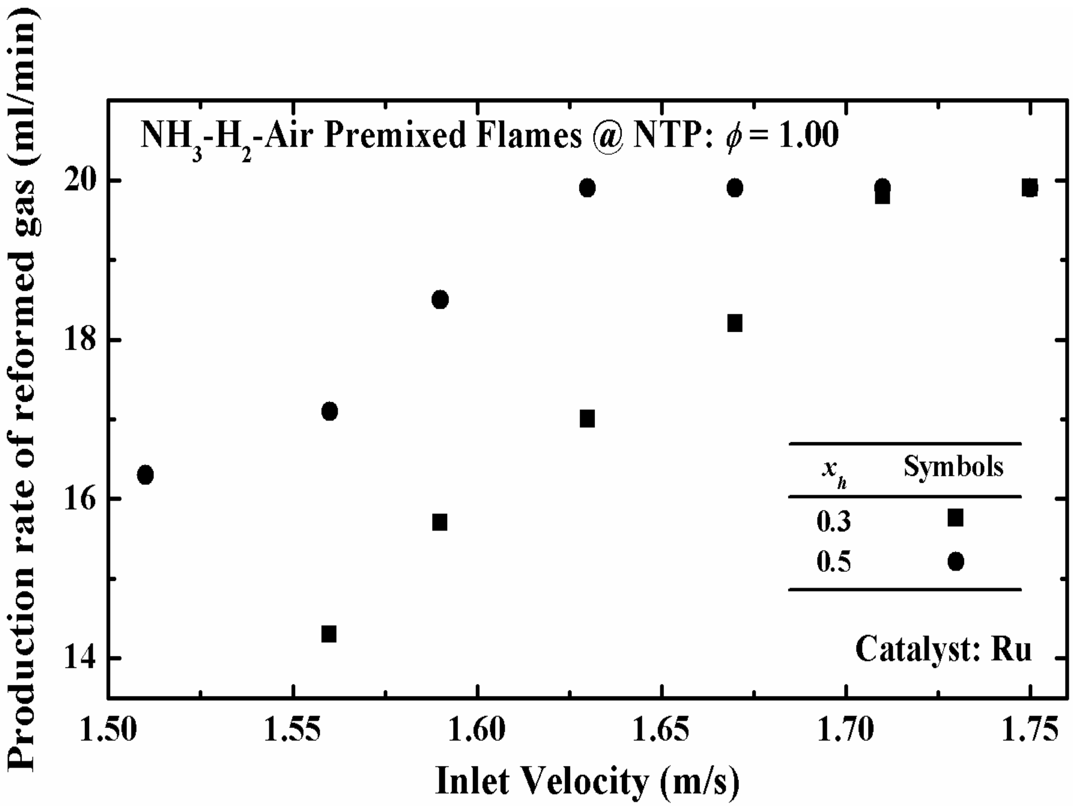
- For Ir and Ru, X_{NH3} decreases with increasing V until V = 3.1 m/s.
- For $Ni/SiO_2/Al_2O_3$, higher temperature condition in the micro-reformer (and hence in the micro-combustor) than that for Ir and Ru is needed.
- The minimum value of unreacted NH_3 mole fraction X_{NH3} = 0.01 is observed at $\dot{m}_f$ = 5.0-10.0 ml/min and V = 3.1-3.7 m/s.



Optimized condition (C_3H_8-air)

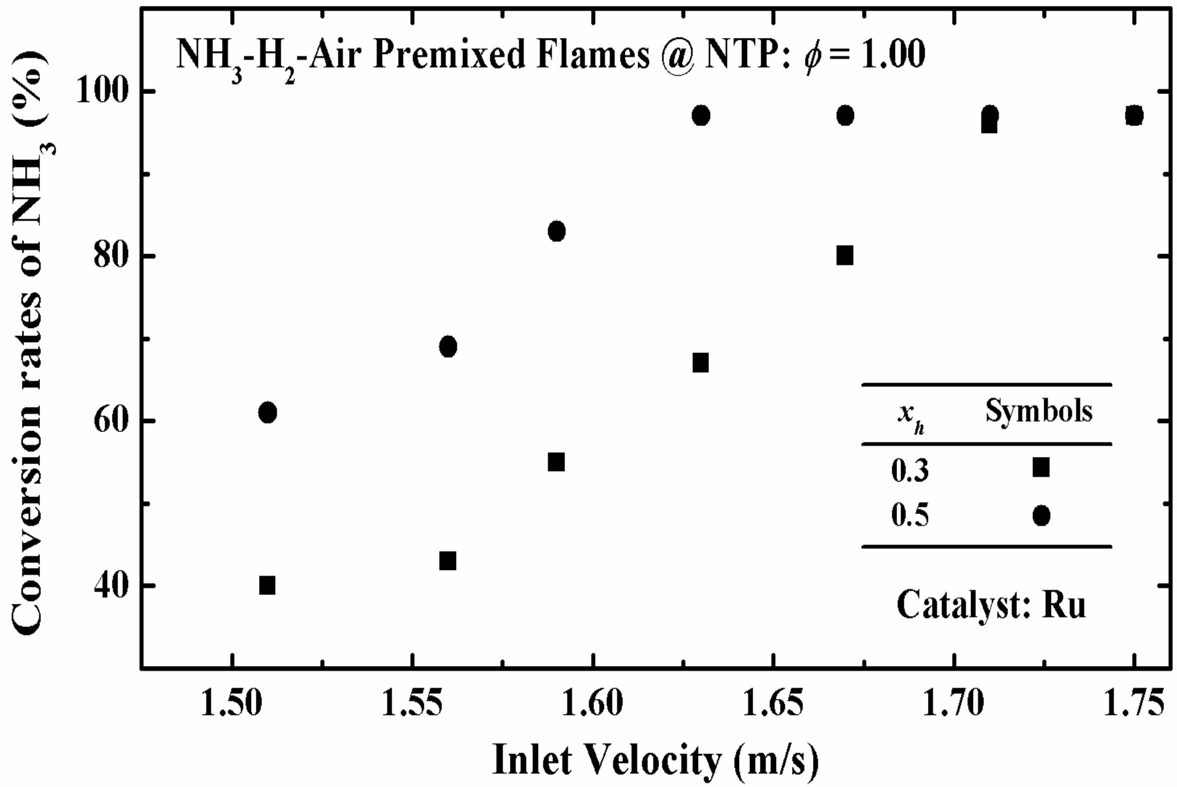
Operation/performance parameters	Values
Materials	Stainless steel (SS304)
Catalyst	Ruthenium (Ru)
Equivalence ratio of premixed propane-air flame (ϕ)	1.0
Micro-combustor inlet velocity (V)	3.1 m/s
Feed rate of ammonia ($\dot{m}_f$)	10.0 ml/min
Production rate of reformed gas ($\dot{m}_r$)	20.1 ml/min = 5.4 W (based on LHV)
Conversion rate of ammonia ($\dot{r}$)	98.0%
Unreacted ammonia mole fraction (X_{NH3})	0.01
Overall system efficiency (η)	13.7%

Production rate of reformed gas: $\phi = 1.0$ (NH_3-H_2-air)



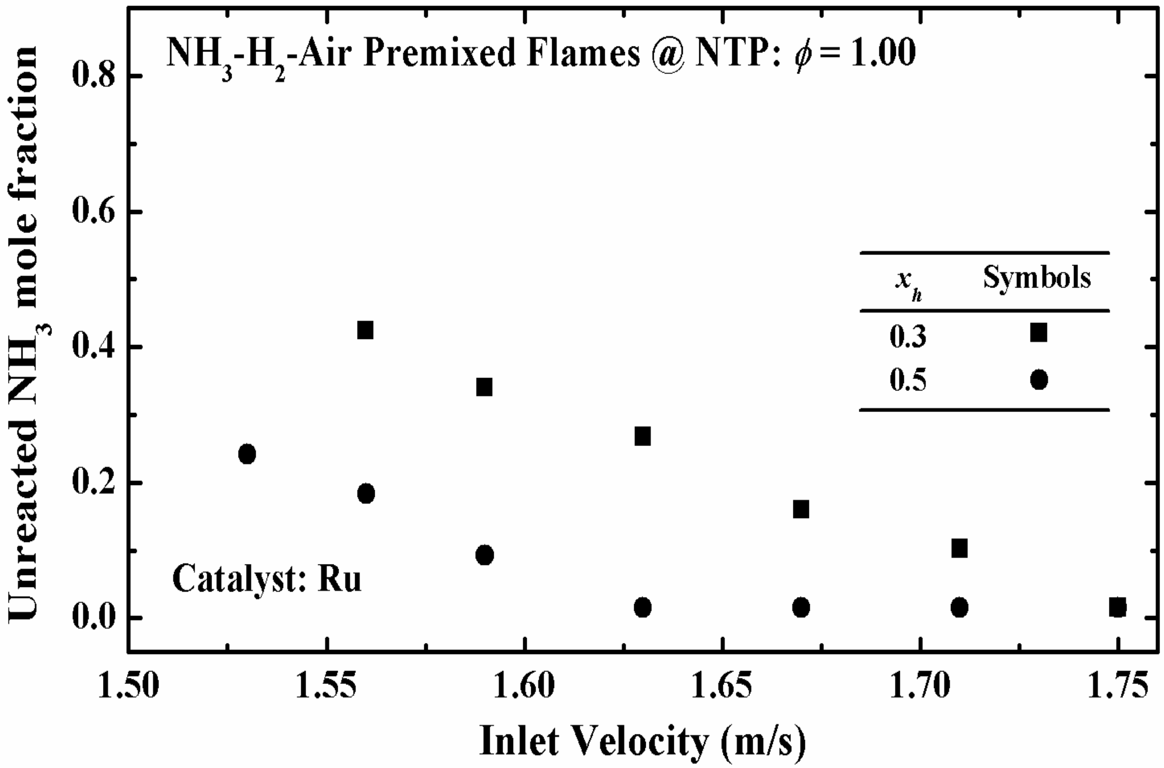
- $\dot{m}_r$ increases with increasing *V* until a certain condition (which decreases with increasing X_h) due to the increased amount of the supplied fuel and then becomes almost constant since flame is stabilized in the micro-combustor, providing the appropriate amount of heat into the micro-reformer regardless of varying *V*.
- The maximum $\dot{m}_r$ = 20 ml/min.

Conversion rate of ammonia: $\phi = 1.0$



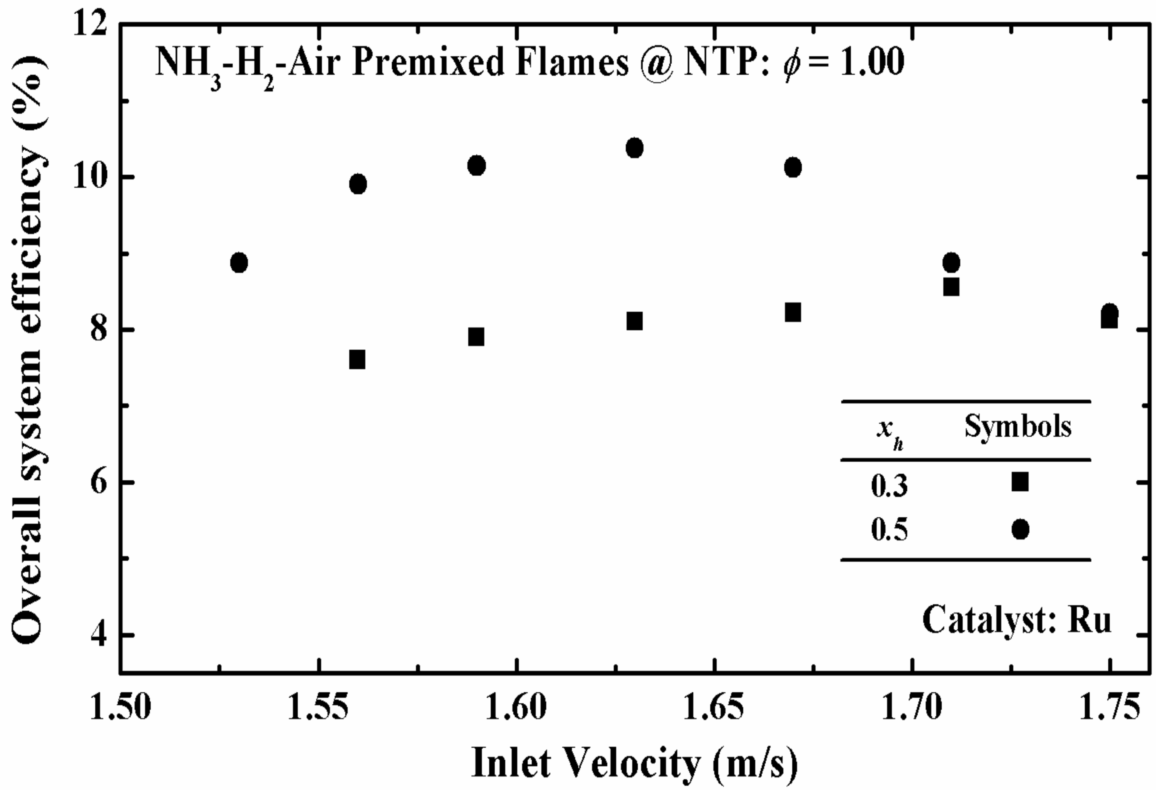
- A tendency similar to $\dot{m}_r$ is observed for $\dot{r}$.
- The maximum $\dot{r}$ = 97%.

Unreacted ammonia mole fraction: $\phi = 1.0$



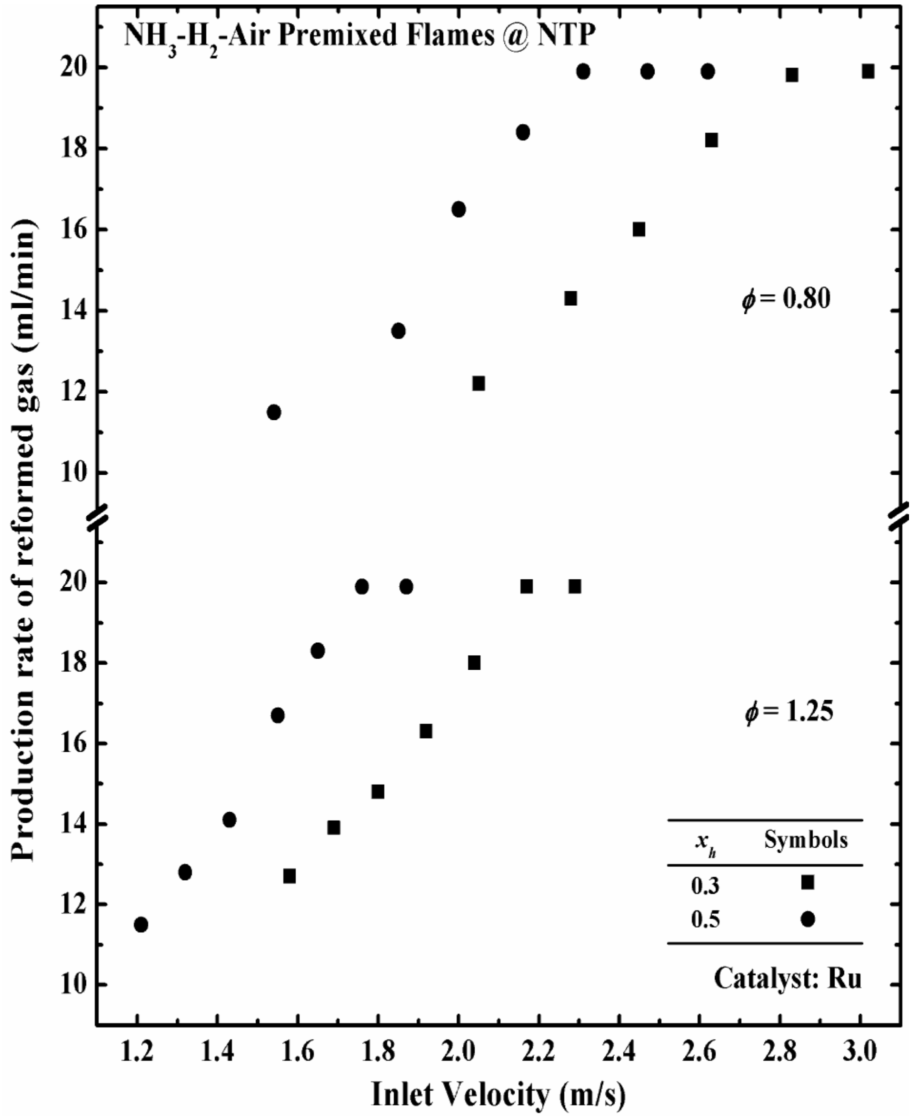
- X_{NH3} decreases with increasing V.
- The minimum X_{NH3} = 0.015.

Overall system efficiency: $\phi = 1.0$



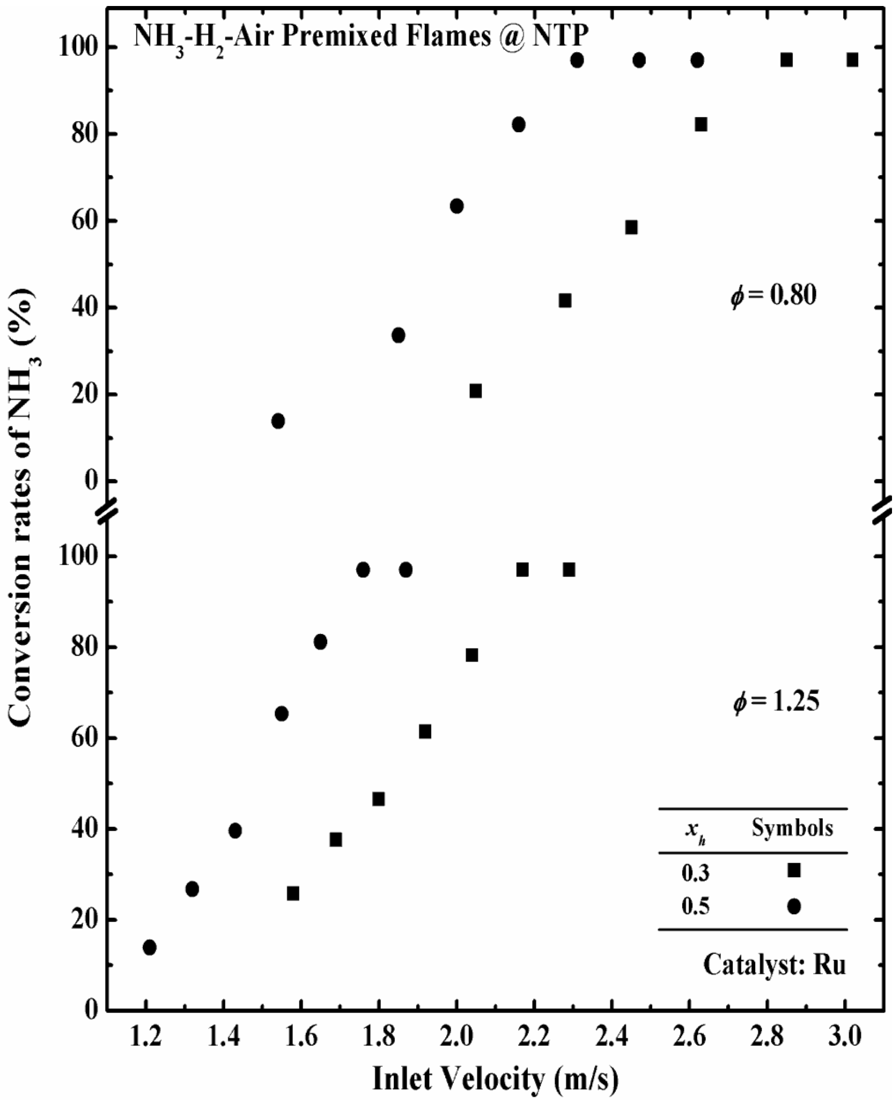
- η increases with increasing V until a certain condition due to the increased amount of the supplied fuel and then decreases since flame is already stabilized in the micro-combustor and thus more enhanced V results in wasting fuel input without increasing hydrogen output.
- The maximum $\eta = 10.4\%$ @ $V = 1.63$ m/s and $X_h = 0.5$.

Production rate of reformed gas: $\phi = 0.8\text{–}1.25$



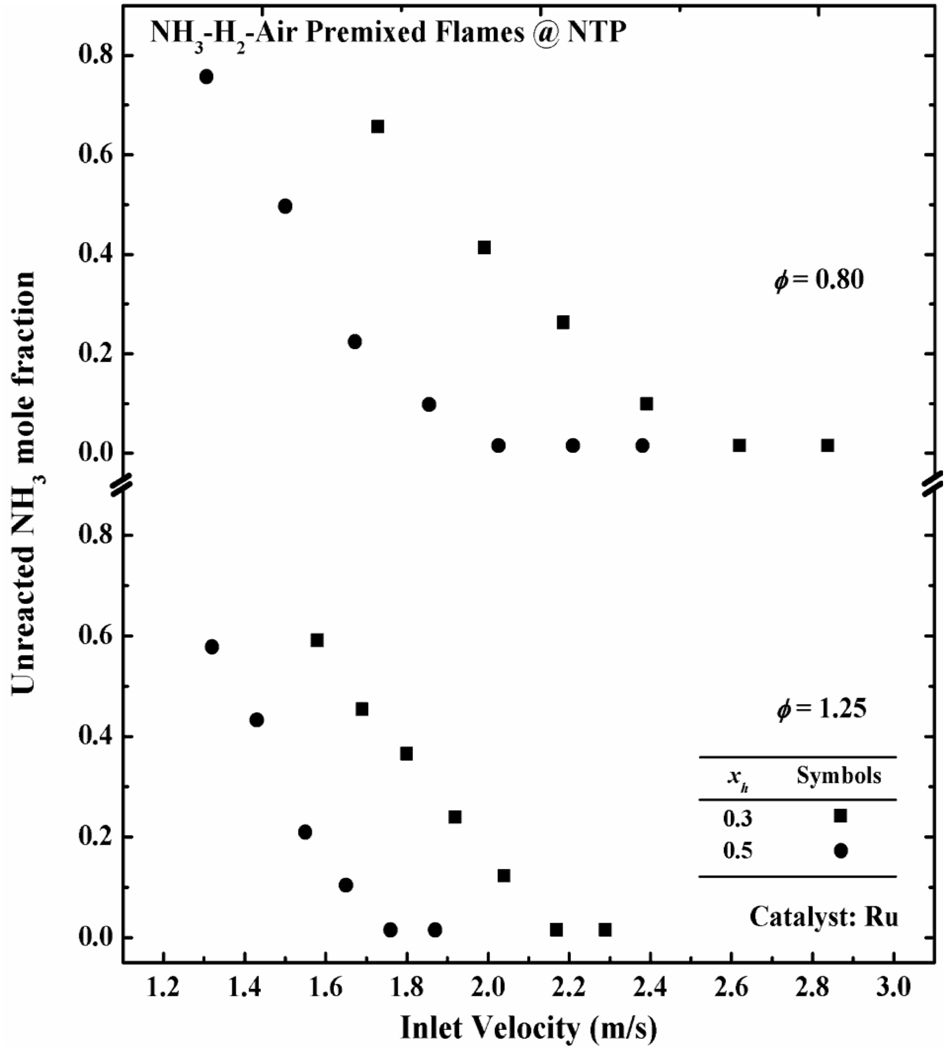
- A tendency similar to that for $\phi = 1.0$ is observed for $\phi = 0.8$ and 1.25.
- The maximum $\dot{m}_r$ is still 20 ml/min.
- However, the *V*s where the maximum $\dot{m}_r$ reaches increase, particularly for fuel-lean condition.

Conversion rate of ammonia: $\phi = 0.8–1.25$



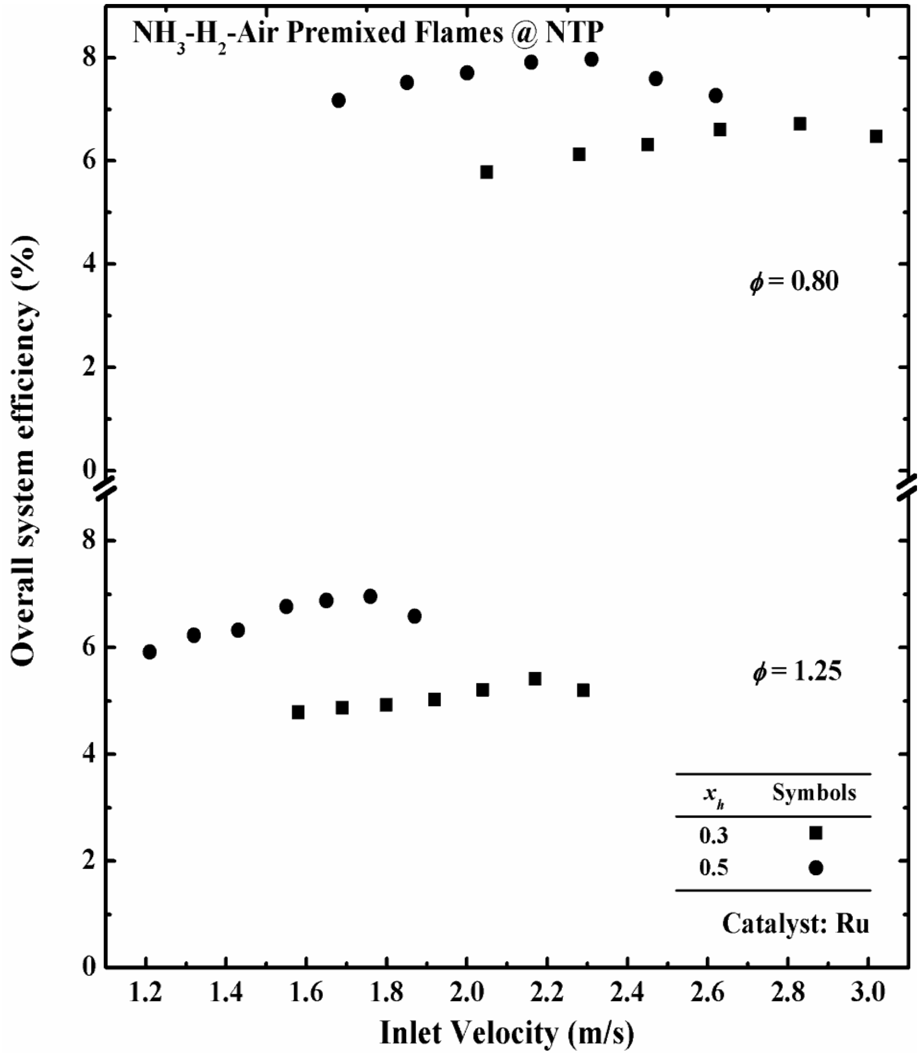
- A tendency similar to that for $\phi = 1.0$ is observed for $\phi = 0.8$ and 1.25.
- The maximum $\dot{r}$ is still 97%.
- However, the *V*s where the maximum $\dot{r}$ reaches increase, particularly for fuel-lean condition.

Unreacted NH_3 mole fraction: $\phi = 0.8–1.25$



- A tendency similar to that for $\phi = 1.0$ is observed for $\phi = 0.8$ and 1.25.
- The minimum X_{NH3} is still 0.015.
- However, the *V*s where the minimum X_{NH3} reaches increase, particularly for fuel-lean condition.

Overall system efficiency: ϕ = 0.8–1.25

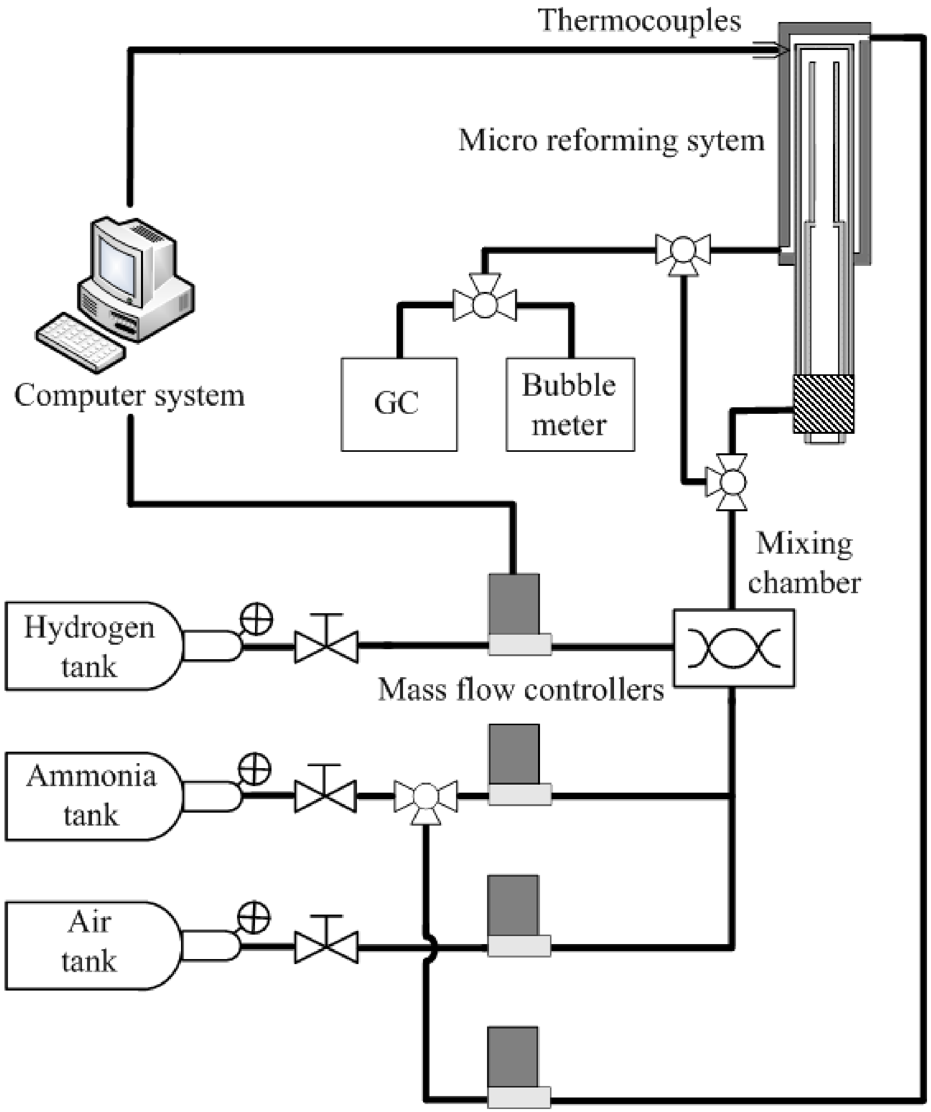


- A tendency similar to that for ϕ = 1.0 is observed for ϕ = 0.8 and 1.25.
- However, η is somewhat reduced, particularly for fuel-rich condition.
- Also, the *V*s where the maximum η reaches increase.

Optimized condition (NH_3-H_2-air)

Operation/performance parameters	Values
Materials	Stainless steel (SS304)
Catalyst	Ruthenium (Ru)
Equivalence ratio of premixed NH_3-H_2-air flame (ϕ)	1.00
Micro-combustor inlet velocity (V)	1.63 m/s
Mole fraction of H_2 in fuel gas (x_h)	0.5
Feed rate of ammonia ($\dot{m}_f$)	10.0 ml/min
Production rate of reformed gas ($\dot{m}_r$)	20.1 ml/min = 5.4 W (based on LHV)
Conversion rate of ammonia ($\dot{r}$)	97.0%
Unreacted ammonia mole fraction (X_{NH3})	0.015
Overall system efficiency (η)	10.4%

Recirculation of reformed gas



- Approximately 48–52% of the total amount of the reformed gas without the recirculation.
- The ammonia conversion rate of 97.0% was still measured.
- Stably working.

Summary

- An annulus-type micro reforming system which consists of a heat-recirculating micro-combustor as a heat source and a micro-reformer surrounding the micro-combustor has successfully produced hydrogen, using ammonia as a fuel for both reforming and burning.

- An optimized feed rate of ammonia was determined by preliminary tests using propane as a fuel for the micro-combustor (10.0 ml/min).

- The production rate of reformed gas and the conversion rate of ammonia increase with the increasing inlet velocity of mixtures *V* until a certain condition since the amount of the supplied fuel increases, intensifying burning in the micro-combustor and enhancing heat transfer into the micro-reformer, and then becomes almost constant since flame is stabilized in the micro-combustor, providing the appropriate amount of heat into the micro-reformer regardless of varying *V*.

Summary

- **The performance of the micro reforming system is enhanced with the increasing amount of substituted hydrogen.**

- **Ru seems to be the most cost-effective among the catalysts considered in the present investigation.**

- **The overall system efficiency increases with increasing *V* until a certain condition due to the increased amount of the supplied fuel and then decreases since flame is already stabilized in the micro-combustor and thus more enhanced *V* results in wasting fuel input without increasing hydrogen output.**

- **Stoichiometric hydrogen-substituted ammonia-air mixtures provide the best performance of the micro reforming system.**

- **Under optimized operating conditions, an overall system efficiency of 10.4% was obtained.**

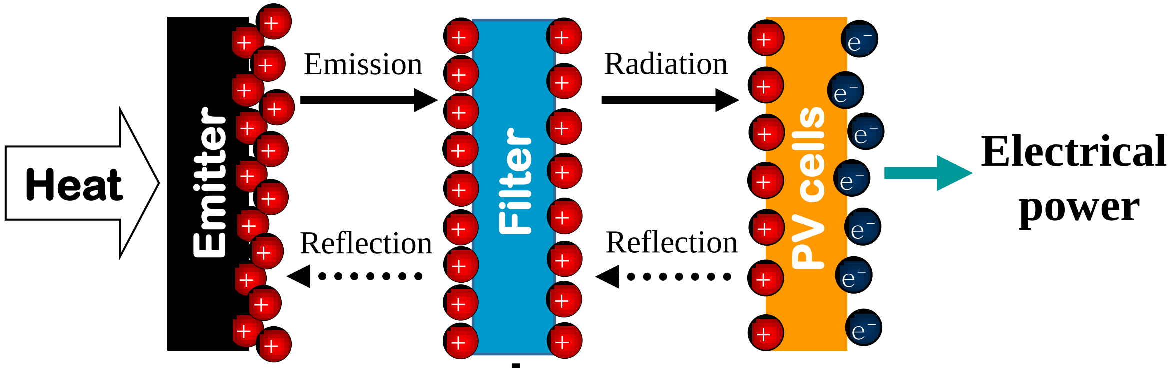
Concluding remarks

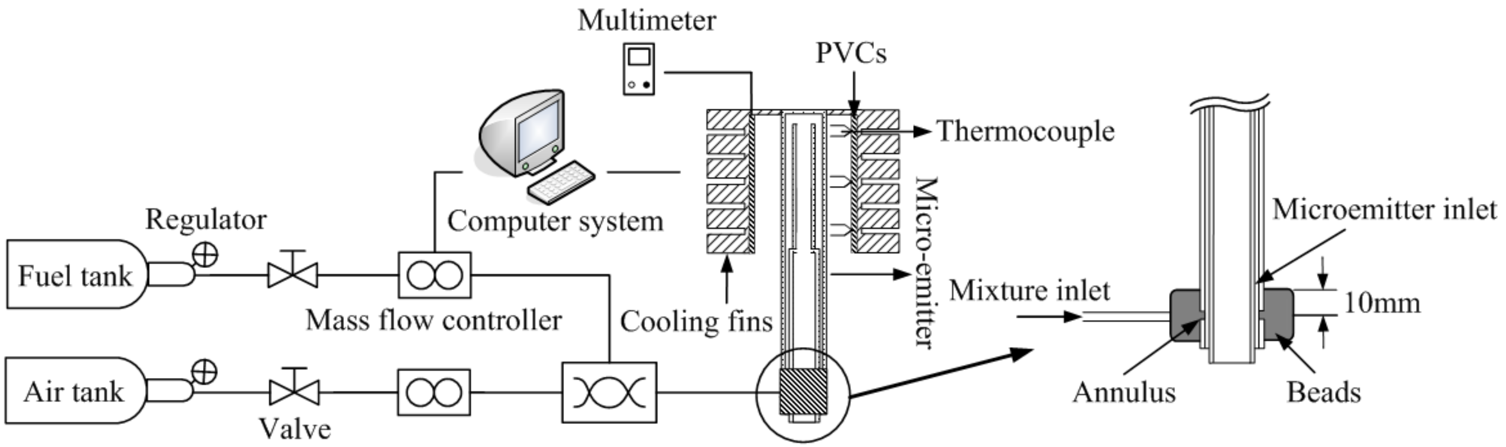
- **Based on the fundamental characteristics of ammonia-fueled flames that were obtained from outwardly-propagating, burner-stabilized and counterflow flame configurations, a micro reforming system integrated with a micro-combustor that reforms and burns ammonia has been successfully designed.**
- **Under optimized operating conditions, the micro reforming system produces 5.4 W (based on lower heating value) of hydrogen with a conversion rate of 97.0% and an overall system efficiency of 10.4%.**
- **This supports the potential of using ammonia as a clean fuel for both reforming and burning in micro reforming systems.**

Further study - applications

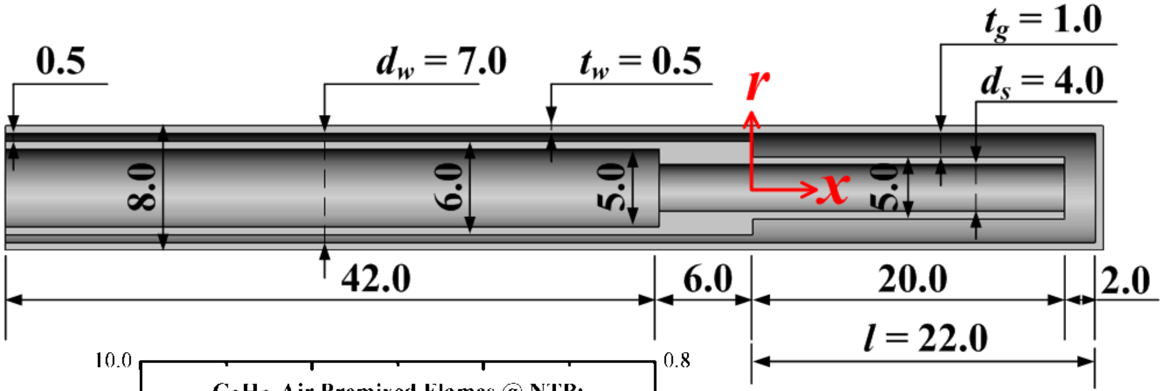
Thermophotovoltaic (TPV) devices

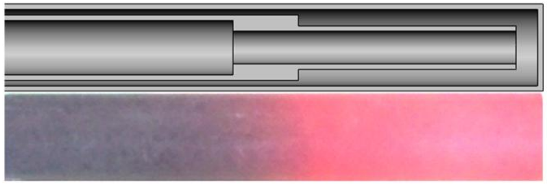
- **A further study on an ammonia-fueled micro thermo-photovoltaic system is also conducted to evaluate the potential of using ammonia in micro power generation systems.**





Thermophotovoltaic (TPV) devices





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